Undergraduate Student Exploration of Parameters Affecting Substitution, Elimination, and Solvolysis Reactions

THESIS

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By

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Abstract

The motivation for this work was the lack of a robust teaching laboratory experiment for a sophomore level organic chemistry course that engaged students in the complexities of substitution, elimination, and solvolysis chemistry. The purpose of this work was to lay a foundation for the creation of such an experiment. As such, this work had two main components: identifying a substrate capable of undergoing all four transformations and producing products which can be easily analyzed on a GC-MS, and designing a teaching lab activity that improves students' understanding of the differences between the four reactions. This work identified (1,2-dibromoethyl)benzene as a suitable substrate due to its multiple reaction sites and its unique structure, which allowed for easy quantitation of most products encountered during this work. While the teaching lab activity did not result in a significant increase in students' ability to correctly answer questions about the material, it did provide valuable insight into how to better structure the activity for future students.

This document is dedicated to all who have enabled this journey, in particular, my family and Dr. Noel M. Paul. Without you, none of this would have been possible.

Acknowledgments

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Field of Study

Major Field: Chemical and Biomolecular Engineering

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Chapter 1: Purpose

The complexity of bimolecular substitution and elimination, and unimolecular solvolysis reactions often results in new organic chemistry students struggling to grasp the important concepts, let alone the subtleties, of the reactions. Generalized mechanisms are shown in Figure 1 below.

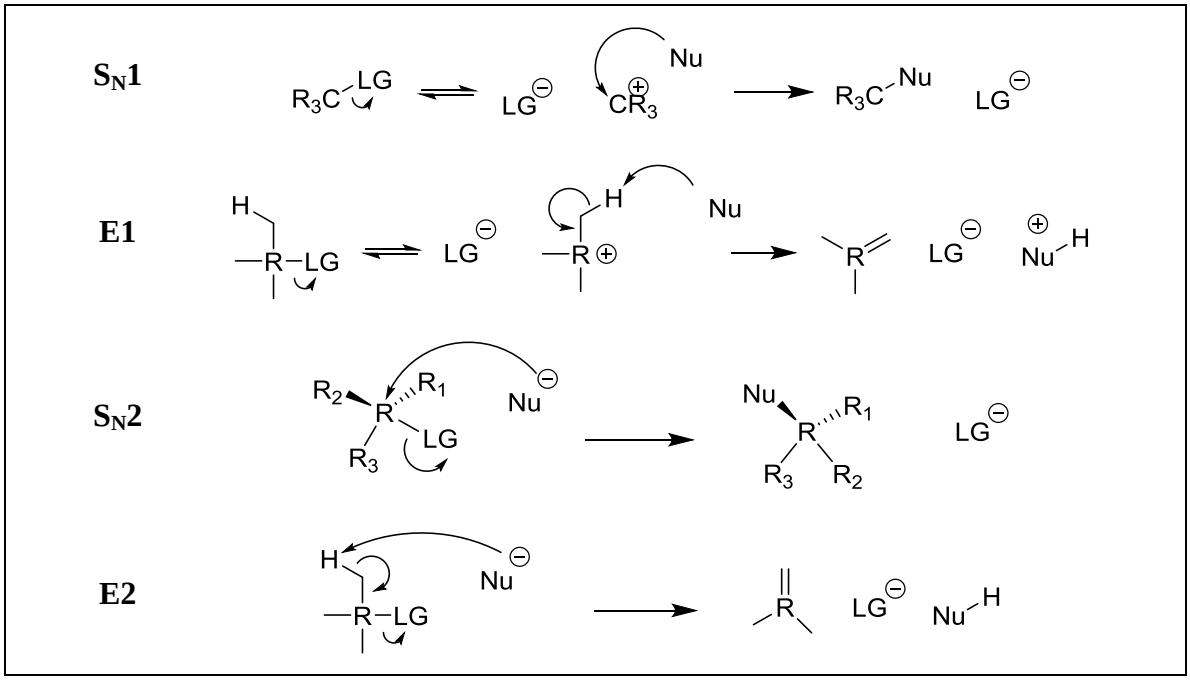


Figure 1. General mechanisms for the four reaction schemes utilized in this research. Solvolysis is comprised of E1 and S_N1 reactions. LG represents a leaving group, and Nu represents a nucleophile.

Substitution and elimination reactions are widely used throughout industrial chemistry for a variety of applications (*1*,*2*,*3*,*4*). Therefore, it is essential that these reactions are well understood by students preparing to enter fields including chemistry, chemical

engineering, pharmacy, medicine, and others. This research aimed to expose students in CHEM 2540 to the relevant reaction mechanisms through an in-lab activity, and increase their understanding of the relevant parameters for each reaction.

These reactions are troublesome for students because the reagents and conditions used are similar, and factors including substrate structure, nucleophile strength, base strength, solvent, temperature, concentration, and reaction time all have a profound effect on a reaction outcome. Understandably, students have difficulty identifying the key parameters that affect the outcome of a given reaction when all of the aforementioned elements must be considered. The ultimate goal of this project is to implement a new experiment for CHEM 2540 which covers the relevant reactions and improves student's learning experience, and this research is the first step toward that goal. The specific learning objectives of the new experiment require students to demonstrate the ability to do the following:

1. Predict the outcome of S_N/E reactions.
2. Identify reaction parameters: reagent structure, reagent chemical properties, equivalents, solvents, temperature, etc. capable of facilitating a specific S_N/E reaction.
3. Analyze data to support conclusions on S_N/E chemical reactivity patterns.

Although experiments that address the relevant mechanisms have been implemented in the teaching laboratory in the past (*5*), a deep investigation of mechanistic selectivity was not possible from students' perspective owing to products that could not be easily

separated and quantitated using chromatographic methods. Therefore, this research had two primary goals:

1. To identify a candidate reagent to be used in a new experiment covering substitution and elimination reactions in CHEM 2540. The criteria this reagent needed to meet included ability to undergo all four main reaction types based on nucleophilicity and base strength (*6*) and produce products which can be easily identified on analytical equipment.
2. To implement a simple activity in CHEM 2540 which exposed students to some of the four main reaction types and tested whether their proficiency at predicting the products of a given set of reaction conditions and identifying the major contributing factors in the formation of the specific products improved after completing the activity.

Chapter 2: Introduction

2.1 Literature Review

Several publications in the literature can be found which aim to guide students in the exploration of substitution, elimination and solvolysis reactions. Pace and Regmi used kinetics to explore the mechanism of the Finkelstein reaction, a thoroughly documented S_N2 (bimolecular substitution) reaction depicted in Figure 2 below. Their substrates consisted of 1-bromobutane, 2-bromobutane, and 1-chlorobutane. Analysis was conducted by measuring the conductivity of the reaction solution (*7*).

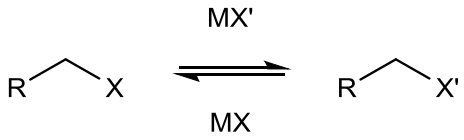


Figure 2. The general scheme of the Finkelstein reaction, which exchanges halogens or pseudohalogens in an S_N2 reaction through treatment with an alkali metal halide.

Wagner and Marshall used a laboratory experiment to explore the S_N1 (unimolecular substitution, one of two reactions comprising solvolysis) mechanism. Their substrate was 2,5-dimethyl-2,5-hexanediol, and the reaction scheme is shown in Figure 3 on page 5.

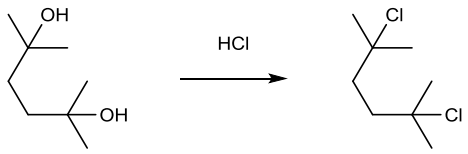


Figure 3. Scheme used by Wagner and Marshall. This reaction follows the S_N1 mechanism. Product analysis required a filtration step, and was carried out by a combination of solubility testing, melting point determination, and thin layer chromatography (TLC). They also suggested the use of Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) as additional methods for product characterization (*8*).

This scheme required product separation through filtration, and analysis was conducted using solubility tests, melting point determination, and thin layer chromatography (TLC). They proposed using Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) as additional characterization methods (*8*).

Wagner and Marshall's experiment also attempted to assess student learning by comparing scores on pre-lab and post-lab quizzes. Each quiz consisted of three questions, one of which required students to identify the S_N1 mechanism. A homoscedastic (unpaired, equal variance assumed) t-test was used to analyze student responses to the pre and post-quizzes and found the mean score was significantly greater on the post quiz (*8*). However, because the data were not matched, it is unknown whether this significant result is due to variability in the students, changes in their understanding of the mechanism, or variability in the other two questions asked on each quiz. Additionally, the post-quiz was administered one week after the experiment, so a large number of factors could have increased a student's ability to identify an S_N1 mechanism during this time, such as studying the material for a midterm exam held the week after the post-quiz. Furthermore, the quizzes each contained two questions presumably not concerning identification of the S_N1 mechanism. Each of these questions introduced additional

variability which was not accounted for in the statistical analysis. Therefore, while it is possible that the laboratory experiment increased students' ability to identify the S_N1 mechanism, this cannot be concluded by the statistical test conducted.

Cabay *et al.* exposed students to the requirement of antiperiplanarity for E2 (bimolecular elimination) reactions, but did not report any result pertinent to students' comprehension of this concept. The substrates used were *trans*-2-methylcyclohexyl tosylate and *cis*-2-methylcyclohexyl tosylate. The reaction scheme is shown in Figure 4 below.

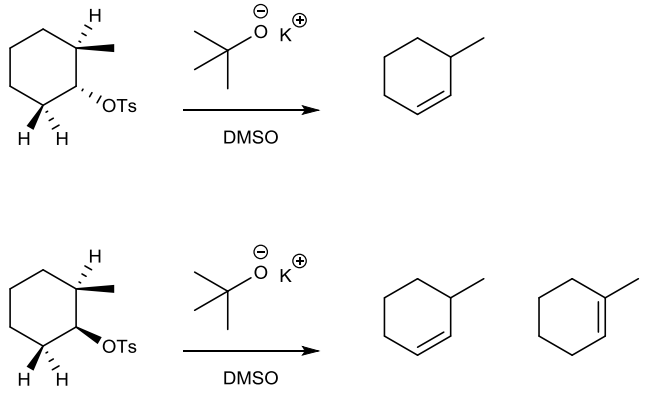


Figure 4. Reaction of trans-2-methylcyclohexyl tosylate with potassium *tert*-butoxide produced only 3-methylcyclohexene, while reaction of cis-2-methylcyclohexyl tosylate with potassium *tert*-butoxide produced both 1-methylcyclohexene and 3-methylcyclohexene. This occurs because carbon 3 on trans-2-methylcyclohexyl tosylate does not have a hydrogen antiperiplanar to the tosylate group (*9*).

Products were analyzed using both NMR and GC. The experiment also required synthesis of *cis* and *trans*-2-methylcyclohexyl tosylate from *cis* and *trans*-2-methylcyclohexanol, which themselves were synthesized due to the high cost of purchasing them commercially (*9*).

Latimer analyzed the product distribution of four reactions that followed both the S_N2 and E2 mechanisms that used 1 and 2-bromopentane as substrates. These reaction schemes are shown in Figure 5 on page 7. The purpose of the experiment was to observe how

sterics affect the nucleophilicity of strong bases. Latimer did not report any information regarding student's comprehension of the material. Additionally, only the elimination products were considered, and characterization was done through GC (*10*).

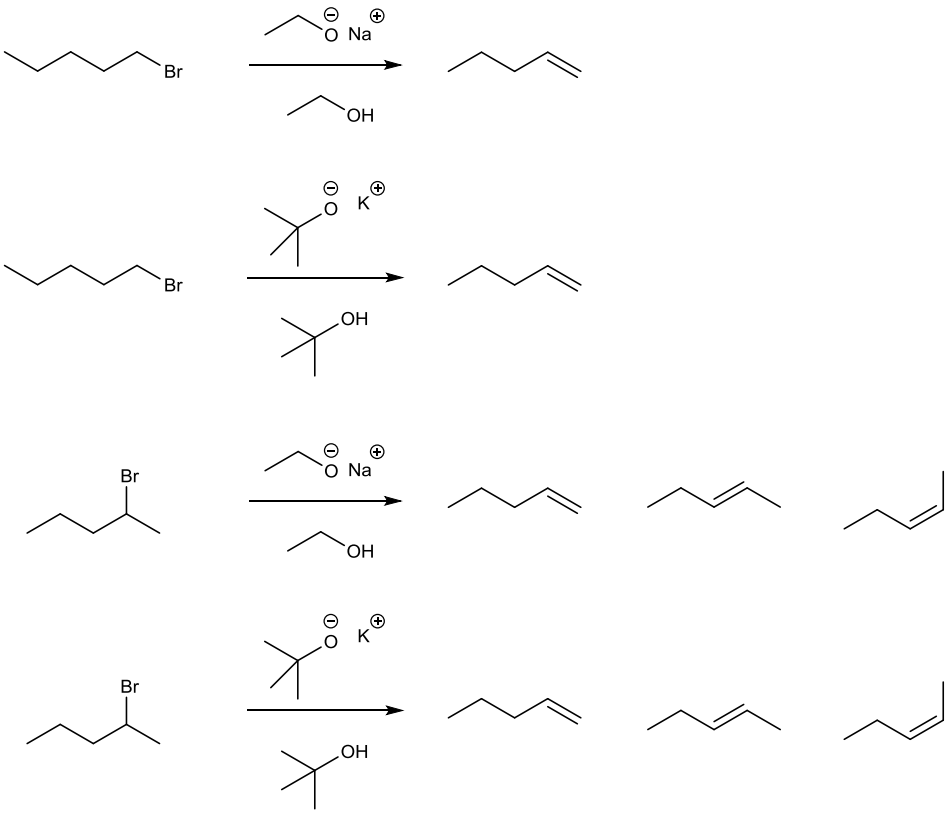


Figure 5. These schemes were used by Latimer's experiment. Some of these reactions may produce substitution products, but these were not considered. While it appears based on the schema that the base used did not impact the reactions, the base did change the relative amounts of the products for reactions with 2-bromopentane (*10*).

Wharry improved on Latimer's experiment by analyzing the substitution products as well as the elimination products, and by adding 2-bromo-2-methylbutane as a substrate and using methanol as a solvent, which thereby examined primary, secondary, and tertiary haloalkanes with increasing degrees of steric hindrance. The reaction schemes used are shown in Figure 6 on page 9. The procedure of the experiment required students to do a

simple extraction, wash, and dry before analysis using a GC. Wharry also suggested incorporating student interpretation of GC FID peaks from their products as a method to include the analytical techniques students learn in sophomore level organic chemistry courses in the experiment, but in the experiment, students were provided with labeled chromatograms. Students then wrote lab reports in groups of six, with each student having performed a different reaction (*11*).

The work outlined in this document seeks to lay the foundation for an experiment which improves upon the ideas described in the literature referenced here.

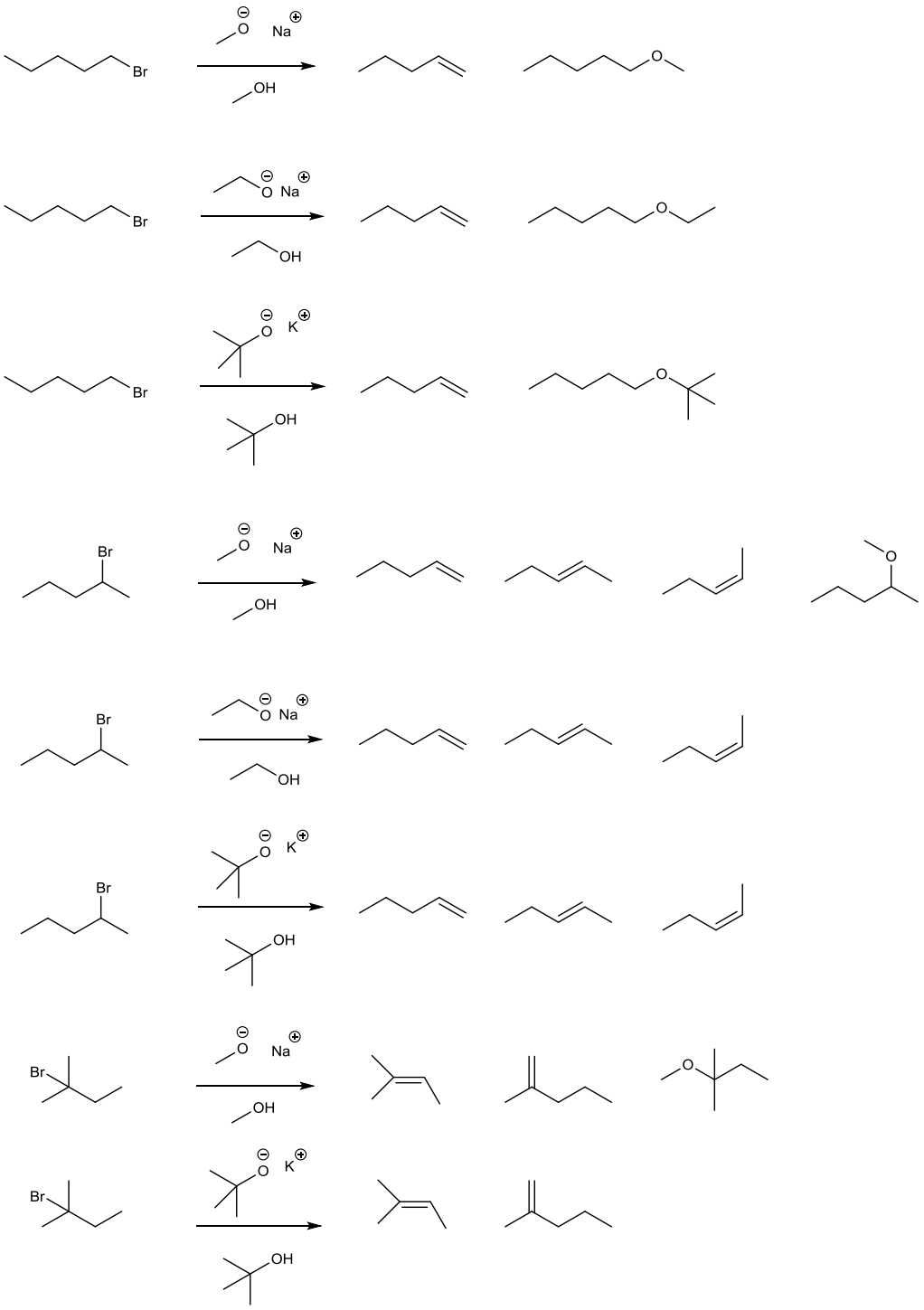


Figure 6. These 8 reactions were used by Wharry to examine the shift between substitution and elimination products with increasing halide degree and increasing steric hindrance of the base.

2.2 Reagent Selection

Gas chromatographic (GC) methods remain the most efficient technique to quantitate student experimental results in the laboratory. Therefore, and ideal starting material for this research needed to yield an array of products having boiling points higher than typical reaction solvents, and yield isomeric products with substantial structural differences, both of these necessary to facilitate the retention on and separation of the product mixture using a chromatography column. An ideal substrate would likely not be a straight-chain alkane because these elute from GC columns very quickly, and peaks could potentially become intermixed with solvent peaks, resulting in a difficult analysis. Aromatic compounds were researched as a potential alternative to the butane, pentane, and hexane derivatives frequently used in the literature (*7*,*8*,*10*,*11*), and several commercially available compounds were identified and are tabulated in Table 1 on page 11. From these compounds, the most promising substrate was selected: (1,2-dibromoethyl)benzene. This compound was selected because of its theoretical flexibility in undergoing the required transformations, and because it was the most economically feasible to use for a course with over 2,000 students in an academic year. With a planned starting amount of approximately 0.1 g per student, reagent cost would be only $115/ academic year (*12*), whereas a similar amount of meso-1,2-dibromo-1,2-diphenylethane would cost in excess of $600 (*13*). As purchased, this reagent is racemic, so inversion of configuration will not be possible directly. Available solvents and nucleophiles were recorded and are tabulated in Table 2 on page 12.

Table 1. The reagents included in this table were all commercially available at the time of the experiment from at least one of the following suppliers: Sigma-Aldrich, Fischer Scientific, and Spectrum. An asterisk indicates bulk purchase was required.

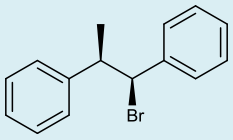
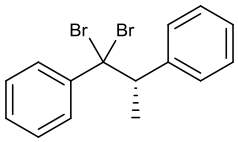
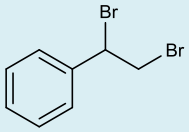
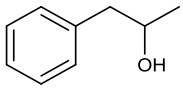
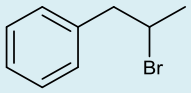
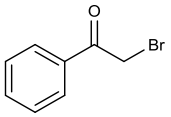
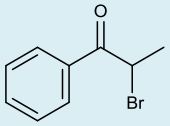
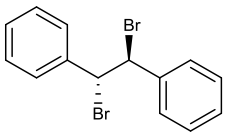
IUPAC [common]	Structure
[(1R,2S)-2-bromo-1-methyl-2-phenylethyl]benzene* [none]	 $C_{15}H_{15}Br$
[(2S)-1,1-dibromo-2-phenylpropyl]benzene* [none]	 $C_{15}H_{14}Br_2$
(1,2-dibromoethyl)benzene [styrene dibromide]	 $C_8H_8Br_2$
1-phenyl-2-propanol [α-methylphenethyl alcohol]	 $C_9H_{12}O$
2-bromo-1-phenylpropane [(2-bromopropyl)benzene]	 $C_9H_{11}Br$
2-bromoacetophenone [phenacyl bromide]	 C_8H_7BrO
2-bromopropiophenone [α-bromopropiophenone]	 C_9H_9BrO
meso-1,2-dibromo-1,2-diphenylethane [stilbene dibromide]	 $C_{14}H_{12}Br_2$

Table 2. Reagents available for reaction schemes. Solvent reflux temperature was included to assist in pairing reactions with solvents based on maximum temperature.

Substrate	**Nucleophile**	**Solvent**	**bp (^{0}C)**
(1,2-dibromoethyl)benzene	potassium *t*-butoxide	ethanol	78.3
	sodium methoxide	acetonitrile (ACN)	81.6
	triphenylphosphine	dichloromethane (DCM)	40
		methanol	64.5
		dimethylsulfoxide (DMSO)	189
		cyclohexane	80.7
		N,*N*-dimethylformamide (DMF)	152
		tetrahydrofuran (THF)	66
		acetone	56.2
		water	100
		1,2-dichloroethane	83
		chloroform	60.5-61.5
		tert-butanol	83

Chapter 3: Experimental Methodology

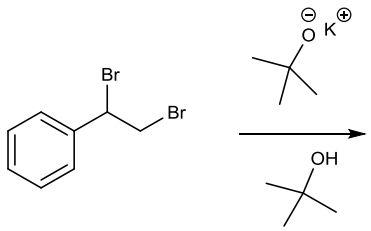
3.1 Reaction Experiments

The experimental setup is shown in Figure 7. All experiments were carried out consecutively with overlapping reaction times such that when one reaction was started, reagents were measured out for the second reaction. Reaction times were all approximately 1 h.

Figure 7. Experimental setup used for reactions.

Reaction conditions and yields were not optimized. Gas chromatography-mass spectrometry (GC/MS) data were acquired using an Agilent Technologies (Santa Clara, CA) 6850 GC equipped with an HP-5MS column (crosslinked 5% PH ME siloxane, 30 m x 0.25 mm I.D. x 0.25 μm film thickness) and a 5975C VL mass-selective detector with triple-axis detector. Ultrapure grade helium was used as the carrier gas in constant flow mode at a flow rate of 0.9 mL/min. The injection port and transfer line temperatures were both 250 °C, and the oven temperature gradient used was as follows: the initial temperature was 50 °C, and was immediately increased to 250 °C at 20.0 °C/min over 20 min (0:00-30:00 min). Anhydrous solvents were purchased from Fischer (methanol, THF, diethyl ether) and were used without further purification. (1,2-dibromoethyl)benzene was purchased from Sigma-Aldrich. The mass spectrometer tune conducted before analyzing data is contained in Figure 36 on page 60. Reference spectra were obtained from NIST 08 Mass Spectral Library (*14*).

The reaction used to generate only E2 products is shown in Scheme 1 below.

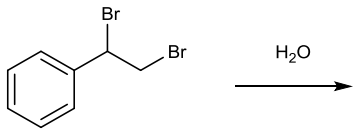


Scheme 1. The steric hindrance caused by the CH_3 groups attached to the central carbon in potassium *tert*-butoxide prevents it from attacking a carbon in (1,2-dibromoethyl)benzene, hence the prediction of only elimination products.

Potassium *tert*-butoxide (0.2242 g, 1.998 mmol) was added to a solution of (1,2-dibromoethyl)benzene (0.1321 g, 0.500 mmol) in *tert*-butanol (15 mL) and the reaction was heated to 50°C for 1 h. A GC-MS sample was run using *tert*-butanol as the solvent.

Tetrahydrofuran (THF) can be used as a substitute for *tert*-butanol in this reaction. However, this will decrease the maximum reaction temperature, and is a more difficult procedure as potassium *tert*-butoxide is not readily soluble in THF.

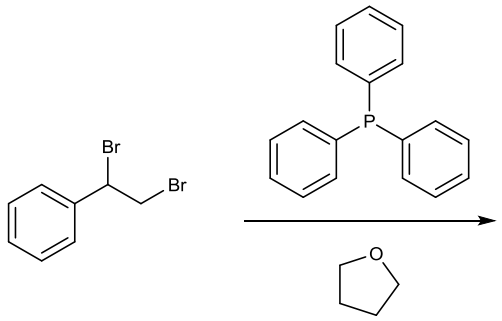
The scheme used to produce only solvolysis products is shown in Scheme 2 below.



Scheme 2. As a weak base and a poor nucleophile, water was expected to produce products of solvolysis through the S_N1 and E1 mechanisms.

(1,2-dibromoethyl)benzene (0.1105 g, 0.4186 mmol) was added to distilled water (20 mL) at 50°C and the reaction was maintained at 50°C for 1 h. The reaction solution was then cooled to 25 °C, and extracted with diethyl ether (10 mL). A GC-MS sample was run with diethyl ether solvent.

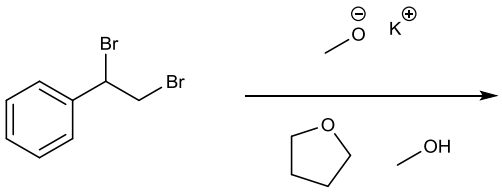
The scheme used to produce only S_N2 products is shown in Scheme 3 on page 16.



Scheme 3. The scheme shown would theoretically produce only S_N2 products because triphenylphosphine is a good nucleophile and a weak base.

Triphenylphosphine (0.4279 g, 1.63 mmol) was added to a solution of (1,2-dibromoethyl)benzene (0.1056 g, 0.400 mmol) in THF (20 mL), and the reaction was maintained at 50°C for 1.2 h. A GC-MS sample was run with THF solvent.

The scheme used to produce substitution and elimination products by the S_N2 and E2 mechanisms is shown in Scheme 4 below.



Scheme 4. This scheme requires a 1:1 mixture of methanol and THF solvent because (1,2-dibromoethyl)benzene is not soluble in methanol, and potassium methoxide is not soluble in THF. Because potassium methoxide is a good nucleophile and strong base, this scheme would produce S_N2 and E2 products.

Sodium methoxide (0.0876 g, 1.622 mmol) was added to a solution of (1,2-dibromoethyl)benzene (0.1065 g, 0.403 mmol) in 1:1 THF - methanol (15 mL total) and the reaction was maintained at 50°C for 0.9 h. The solvent components must be well-

mixed prior to adding reagents. A GC-MS sample was run with 1:1 THF-methanol as solvent.

3.2 Student Comprehension Experiment

This work was completed under IRB approval 2015E0134. The experiment to test students' comprehension of parameters pertinent to substitution, elimination, and solvolysis was structured to have three components: a pre-activity quiz, a group activity, and a post quiz in that order. Students' responses to questions on the three components were used as the best available indicator of their knowledge. The experiment was designed to not give students feedback on their pre-quiz submission before they took the post quiz. This was done to prevent the variation in students' choice of whether to examine their pre-quiz results from impacting the experiment. Three different versions of the materials were used. Background material and data from one of the reactions performed were also provided. The reaction of (1,2-dibromoethyl)benzene with triphenylphosphine in THF was not used as an example because the results it produced could not be resolved on the instrument. For more details about the reaction results, see Chapter 4: Results and Discussion. An example of one of the three quiz versions is shown in Figure 8 – Figure 13. Instructions for teaching assistants are included in Figure 27 in Appendix A: Documents for Lab Experiment. The versions were randomly assigned to each class section to minimize the organizational burden for the teaching staff. Each version presented a reaction of the same type for the data set, pre-quiz, and discussion activity, while the post-quiz tested knowledge of a complimentary reaction. Suggested modifications to this procedure and the documents are presented in Chapter 6:

Recommendations. Students completed the quizzes individually, and the discussion activity in groups of approximately four by lab bench. Multiple benches were combined to form groups in sections with low enrollment.

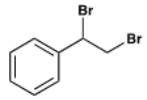
CHEM 2540 – SP15

Introduction to S_N/E Activity

Today in Laboratory, you have the opportunity to participate in an educational study. Students can earn up to ten (10) points of extra credit by working in groups to analyze data and answer discussion questions pertaining to a specific substitution/elimination reaction. The study includes a quiz before and after the discussion activity, and students will have the choice to opt out of the study and still earn extra credit for their discussion.

Focus of the Activity

Differentiating between substitution and/or elimination outcomes in reactions of alkyl halides is a significant problem-solving activity for students in the latter half of Organic Chemistry Lecture I. Though the structure of the alkyl halide dictates reactivity to a large degree, it is the reaction conditions that offer the greatest diversity in potential product formation. In this activity, students will be given a complete set of data for the reaction of (1,2-dibromoethyl)benzene under a specific



(1,2-dibromoethyl)benzene

set of conditions and students will be asked to work together to interpret the data and answer related discussion questions.

The data that is presented here was obtained using Mass Spectrometry detected Gas Chromatography (GC-MS).

Some Helpful Definitions

An **alkyl halide** is a molecule that contains a bond between an sp^3-hybridized carbon atom and a chlorine, bromine, or iodine, which can act as a **leaving group** when this bond is broken to form a halide anion. The carbon bonded to the leaving group is often referred to as the **alpha carbon**, and and carbons directly bonded to the alpha carbon are referred to as **beta carbons**. The hydrogens attached to the beta carbon, are referred to as **beta hydrogens**.

A **nucleophile** is an atom (in a molecule) with a lone pair available for bonding to an atom other than hydrogen. Nucleophiles are considered "*good*" if the lone pair is on (a) a negatively charged, smaller element (H, C, N, O), (b) a larger halide anion (Cl, Br, I), or (c) other larger elements (P, S, Se) that are either neutral or negatively charged. Some "poor" nucleophiles are (a) the neutral oxygen atoms in water, alcohols, and ethers, (b) oxygen anions that are highly resonance stabilized, such those in sulfate, phosphate, and nitrate, (c) neutral halides atoms, and (d) any lone pair on an atom with a large number of bulky groups.

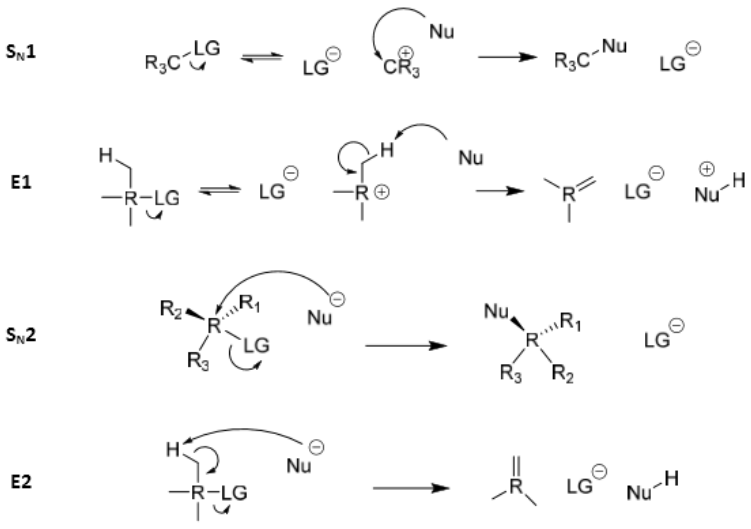
A **base** is an atom (in a molecule) with a lone pair available for bonding with a hydrogen atom. Bases are considered "*strong*" if the lone pair is on a negatively charged, smaller element (H, C, N, O) and is not highly resonance stabilized. Bases are considered "*weak*" if the lone pair is on a neutral atom of any size

A **substitution** reaction is observed when a nucleophile replaces a leaving group on a carbon atom. A **unimolecular nucleophilic substitution** reaction, or **S_N1 reaction** takes place through a carbocation intermediate generated through the loss of the alpha carbon's leaving group first, and

Figure 8. Page 1 of the introductory material which was given to all students who participated in the experiment.

subsequent attack of the carbocation by any nucleophile. A **bimolecular nucleophilic substitution** reaction, or **S_N2 reaction** takes place through the direct displacement of a leaving group on the alpha carbon by a good nucleophile, and is only fast when there is a low steric barrier for that new bond to form.

An **elimination** reaction is observed when groups on adjacent atoms are removed and replaced with a pi-bond. A **unimolecular elimination** reaction, or **E1 reaction** takes place through a carbocation intermediate generated through the loss of the leaving group first, and subsequent deprotonation of a beta-hydrogen atom by any base to give a new carbon-carbon pi-bond. A **bimolecular elimination** reaction, or **E2 reaction** takes place through the simultaneous deprotonation of a beta hydrogen atom and loss of the alpha carbon's leaving group to give a new carbon-carbon pi-bond, and is only fast when the dihedral angle between the alpha leaving group and beta hydrogen is 180°, known as anti-coplanar or anti-periplanar.



Generalized Substitution and Elimination Mechanism Pathways

Figure 9. Page 2 of the introductory material which was given to all students who participated in the experiment.

S_NE Activity – Data Set

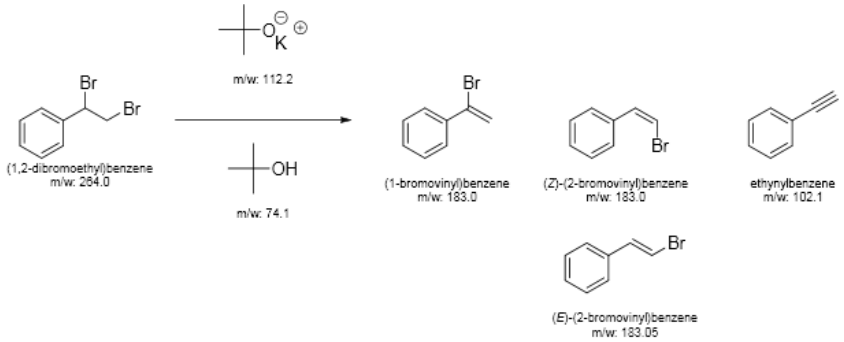


Table 1: Reagent table for reaction 1.

	Reagent	Mass (g)	MW	mmol	ε
T = 50°C, Reaction duration: 66 min	(1,2-dibromoethyl)benzene	0.1321	263.96	0.500	1
	Potassium t-butoxide	0.2242	112.21	1.998	4
	Solvent: t-butanol		74.12		

Table 2: GC peaks for reaction 1.

Peak	Identity	t_R (min)	% comp
1	acetylene (a.k.a. ethynylbenzene)	3.546	12.475
2	(1-bromoethenyl)benzene	5.486	83.360
3	(2-bromoethenyl)benzene	5.972	4.165

1

Figure 10. Data set 1 was the E2 reaction.

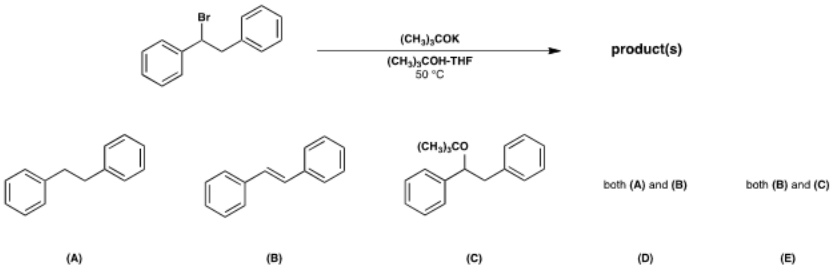
S_NE Activity - Pre-Quiz

CHEM 2540 – SP15

Print Your Name Here *OSU.number*

Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

1. **Predict the Product**. Select the product outcome (Letters A-E) for the reaction shown:



2. **Explain Your Choice**. Given the conditions above, explain your product selection.

Pre1

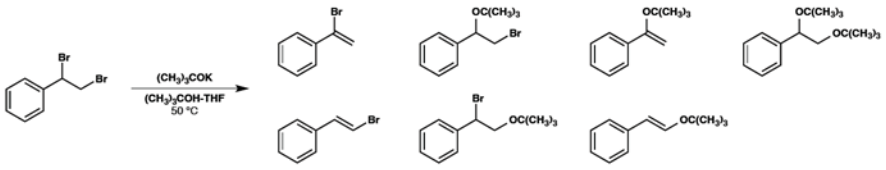
Figure 11. Pre-quiz 1 tested students' knowledge about the E2 reaction.

S_N/E Activity – Discussion Questions

CHEM 2540 – SP15

Your Names *Your Section* *Your Lab/TA*

Learning Objective: Use reaction data to answer questions about S_N/E chemical transformations.



1. Using the data table for the reaction shown, can you determine which of the proposed products above were actually observed? Circle those structures. Were there any products formed that were not listed above? If so, draw the structure(s) above to the right.

2. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a good or bad nucleophile? Explain your reasoning.

3. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a strong or weak base? Explain your reasoning.

4. Can you determine the mechanism(s) that occurred to yield the observed products of the reaction? For each mechanism listed, explain how you determined it did or did not occur.

   S_N2:

   S_N1:

   E2:

   E1:

5. What explains the identity of the major component of this reaction mixture?

D1

Figure 12. Discussion activity 1 also focused on E2 reactions.

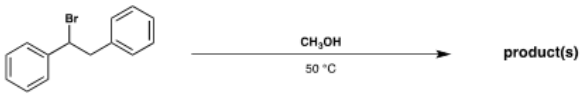
S_NE Activity - Post-Quiz

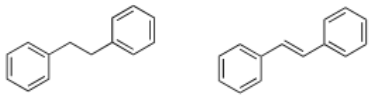
CHEM 2540 – SP15

Print Your Name Here *OSU.number*

Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

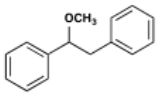
1. **Predict the Product**. Select the product outcome (Letters A-E) for the reaction shown:





(A)

(B)



(C)

both **(A)** and **(B)**

(D)

both **(B)** and **(C)**

(E)

2. **Explain Your Choice**. Given the conditions above, explain your product selection.

Post1A

Figure 13. Post-quiz 1 tested students' knowledge of solvolysis.

Each quiz was scored out of a total possible four points each. Two points were possible on the predict-the-product part of the quiz, and two points were available for the explanation of choice. For pre-quiz 1 and post-quiz 2, 2 points were awarded for only selecting the correct product, option B. One point was awarded for selecting a choice with the correct product and an incorrect product, represented by option D and option E. For pre-quiz 2 and pre-quiz 3, and post-quizzes 1 and 3, 1 point was awarded for selecting a single correct product, option B or option C, and two points were awarded for selecting both correct products, option D. For all three versions, points were earned for the explanation based on the general guideline in Table 3 below.

Table 3. Score criteria for the explanation portion of the quiz. This rubric was used for both the pre and post-quizzes.

Points	**Criteria**
2	a complete explanation which specifically identified the mechanism(s)
1.5	a minor error in the explanation, or not explicitly identifying the mechanism(s)
1	half correct explanation, missing key contributor/only explaining one product
0.5	incorrect explanation except for one minor correct statement
0	completely incorrect solution

Chapter 4: Results and Discussion

4.1 Reaction Experiments

Products produced by Scheme 1 are shown in Figure 14 below. Peak identities for the total ion count (TIC) are tabulated in Table 4, below, and the TIC chromatogram is shown in Figure 15 on page 27. The area percent report is included as Report 1 on page 60.

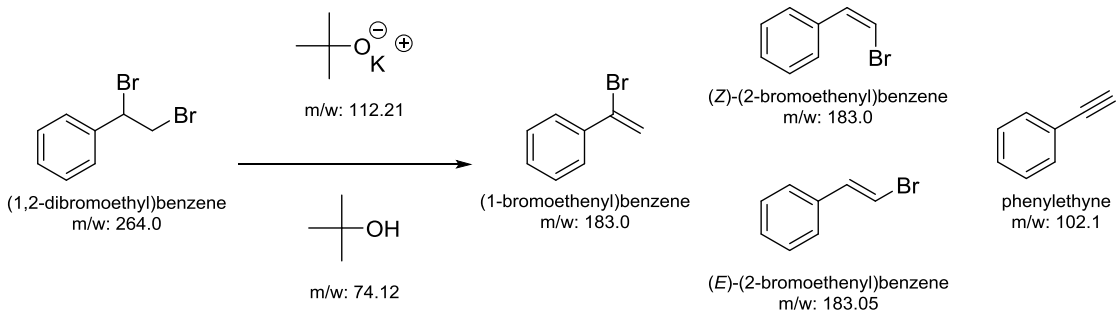


Figure 14. Products produced by Scheme 1.

Table 4. GC peaks for Scheme 1. Peaks are labeled on the TIC for the scheme.

Peak	Identity	t_R (min)	% comp
1	phenylethyne	3.546	12.475
2	(1-bromoethenyl)benzene	5.486	83.360
3	(2-bromoethenyl)benzene	5.970	4.165

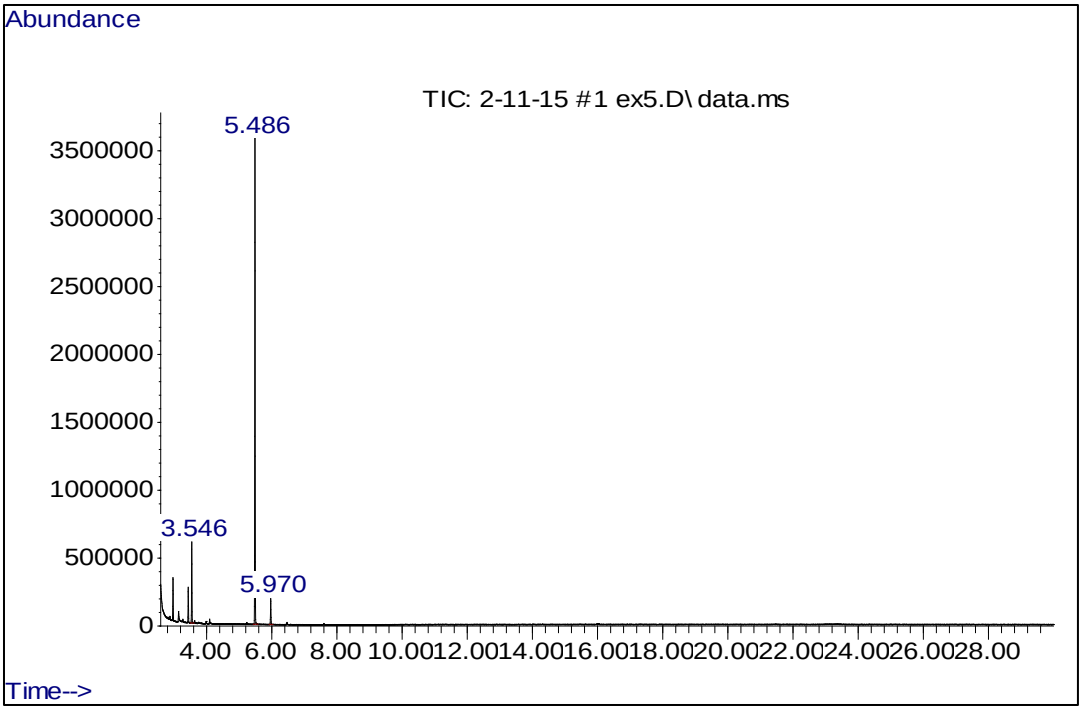


Figure 15. TIC for Scheme 1.

The reaction described in Scheme 1 yielded four products: (1-bromoethenyl)benzene, (*Z*)-(2-bromoethenyl)benzene, (*E*)-(2-bromoethenyl)benzene, and phenylethyne. The (*Z*)- and (*E*)-isomers of (2-bromoethyenyl)benzene did not resolve using the GC method described; however, it was assumed that both were present, and the isomers were treated together in the analysis. In contrast to the Hofmann rule, which states a hindered base will remove the most easily accessible proton, (1-bromoethenyl)benzene was produced in a significantly greater amount than (2-bromoethenyl)benzene. Mass spectra for the peaks and reference spectra for the compounds can be found in Figure 37 – Figure 42 in Appendix B: Data and Reference Spectra.

Products produced by Scheme 2 are shown in Figure 16 on page 28. Peak identities for the TIC are tabulated in Table 5 on page 28 and the TIC is shown in Figure 17 on page 29.

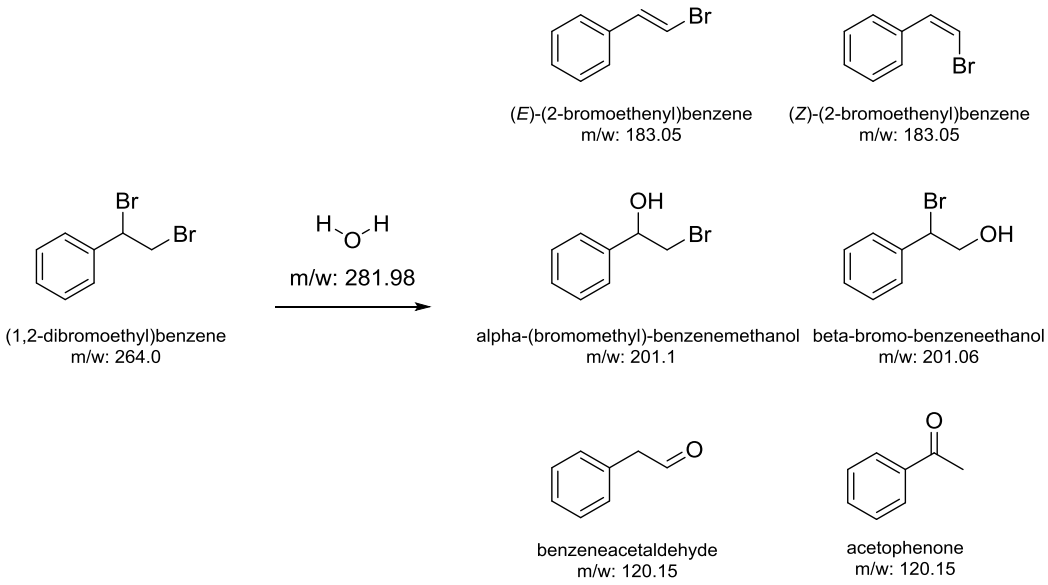


Figure 16. Identified products produced by Scheme 2. An important phenomenon to note is at least four of these products were produced through carbocation formation at the secondary bromine. This occurred because carbocation formation on the secondary carbon is much more stable than carbocation formation on the primary carbon (*15*). In fact, further analysis will show all of these products were formed through carbocation formation at the secondary carbon.

Table 5. GC peaks for Scheme 2. Products marked with an asterisk in the table were produced from an unknown reaction.

Peak	**Identity**	**t_R (min)**	**% comp**
1	styrene*	3.640	2.07
2	benzeneacetaldehyde	4.666	0.25
3	acetophenone	4.828	1.12
4	(2-bromoethenyl)benzene	5.971	0.27
5	ß-bromo-benzeneethanol	6.877	0.23
6	α-(bromomethyl)-benezenemethanol	6.924	3.34
7	(1,2-dibromoethyl)benzene	7.457	91.37
8	BHT	7.874	1.34

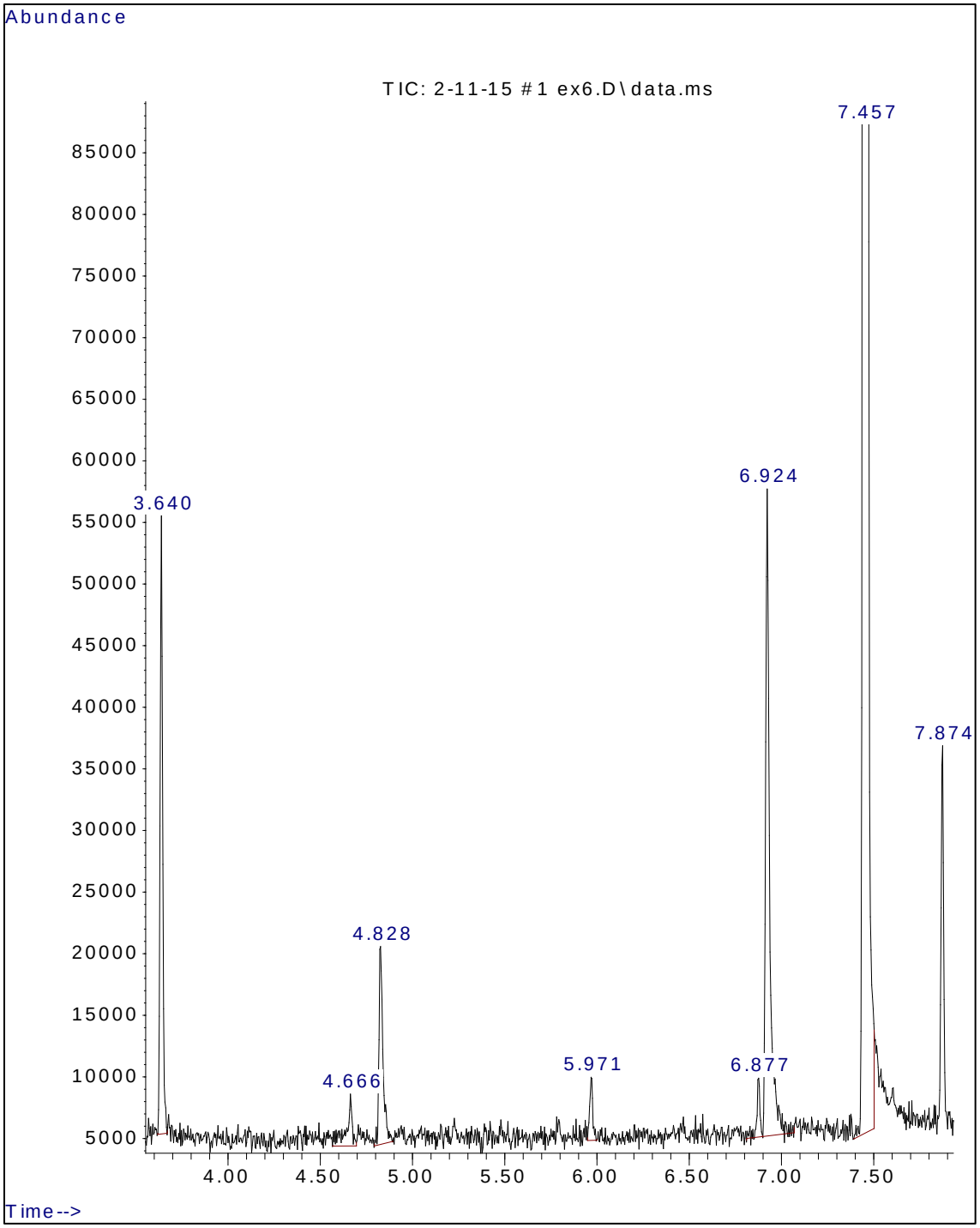


Figure 17. TIC for reaction 2.

Although most of the starting material was unreacted after the reaction time, a rich product distribution was observed. Four out of the five products were formed through a carbocation on the secondary bromine carbon. This can be determined because the secondary bromine has been removed from four of the products. Further information about the reaction mechanisms that occurred can be elucidated from the structure of the products. (2-bromoethenyl)benzene was formed by an E1 reaction at the secondary carbon. While it may initially appear that α-(bromomethyl)-benzenemethanol was formed by an S_N1 reaction at the secondary site, and ß-bromo-benzeneethanol was formed by an S_N1 reaction at the primary site, this was likely not the case. First, the formation of a primary carbocation is extremely unlikely (*16*). Furthermore, the secondary bromine has an inductive effect, further drawing electron density from the primary carbon, which casts additional doubt on the possibility of this reaction path (*17*). However, this does not cast doubt on identification of the product as ß-bromo-benzeneethanol, even though a reference mass spectrum for ß-bromo-benzeneethanol was not found during an exhaustive literature search. It is likely that peak 5 is ß-bromo-benzeneethanol for several reasons. Peak 5 differs from peak 6 in retention time by only 3 seconds. Peak 6 is α-(bromomethyl)-benzenemethanol, which is highly similar in structure to ß-bromo-benzeneethanol; hence their retention times would not be expected to differ significantly. Additionally, examination of the mass spectrum for peak 5, Figure 50 on page 76 in Appendix B:, shows the m/z peak at 184.7, which is an OH fragment difference in mass from ß-bromo-benzeneethanol. The mass spectrum also exhibits peaks for the bromine ion and m, m+2 peaks at 124.8, which is 77 less than the mass of 201.06. The proposed mechanism for both of these products formation is shown in Figure 18 on page 31.

Similar mechanisms have been reported in the literature for dehalogenation reactions in the presence of a nucleophile (*18*). The ratio of these two products in the chromatogram indicates the nucleophile is more readily attacking the primary carbon instead of the secondary carbon. While this is the opposite of what might be expected (*19*), based on the product ratio for elimination on the primary carbon verses elimination on the secondary carbon in Scheme 1, it is not altogether unsurprising that deviation from the rule is observed here as well.

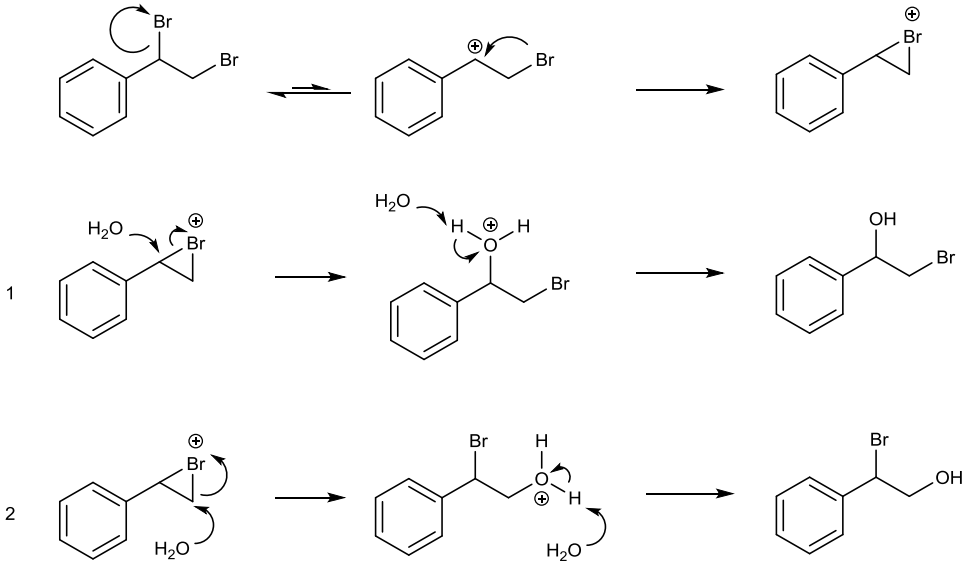


Figure 18. Mechanism for the formation of ß-bromo-benzeneethanol and α-(bromomethyl)-benzenemethanol. The bromonium ion mechanism has been reported in literature as a method of dehalogenation in the presence of a nucleophile (*18*).

Benzeneacetaldehyde formed through an E1 reaction on ß-bromo-benzeneethanol followed by keto-enol tautomerization. α-(bromomethyl)-benzenemethanol is likely a terminal product because hydroxide will not act as a leaving group, and a primary carbocation will not form on the molecule to allow for further reaction. Peak 8 is butylated hydroxytoluene (BHT). The presence of BHT in the chromatogram can likely be attributed to its use as an inhibitor in the diethyl ether solvent used (*20*). Mass spectra

for the peaks and reference spectra are included as Figure 43 – Figure 54 beginning on page 69.

Products produced by Scheme 3 are shown in Figure 19 below. Peak identities for the TIC are tabulated in Table 6 below. The TIC and two close-up views are shown in Figure 20 – Figure 22 starting on page 34.

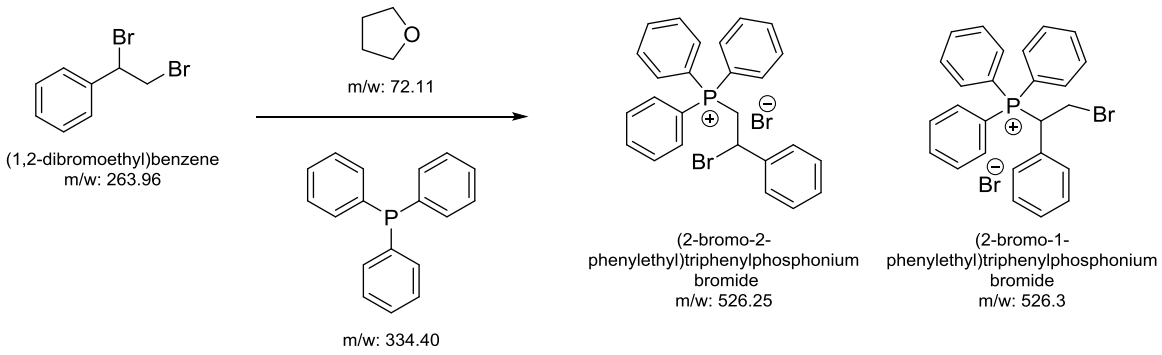


Figure 19. Products of reaction Scheme 3.

Table 6. Two peaks from Scheme 3 could not be identified. Several unexpected products were also observed, although the amounts formed were near to negligibly small. The area percent report can be found in Report 3 on page 81.

Peak	**Identity**	**t_R (min)**
1	tetrahydro-2-furanol	3.040
2	styrene	3.642
3	(1-bromoethenyl)benzene	5.483
4	(2-bromoethenyl)benzene	5.970
5	(1,2-dibromoethyl)benzene	7.457
6	unknown	10.825
7	triphenylphosphine	11.921
8	phosphonium salts	16.083

The mass spectra and reference spectra where applicable can be found in Figure 55 – Figure 67 starting on page 82. The data from Scheme 3 was not used in the teaching

laboratory experiment because many of the peaks were difficult to positively identify. This reaction was expected to be potentially difficult to analyze because the products are high molecular weight polar salts, which are expected to be difficult to volatize. The trace amounts of elimination products were not unexpected, but were present in such small amounts that they were considered negligible.

The identity of peak 1 is tetrahydro-2-furanol, which is a derivative of THF. This species was also present in the product sample for Scheme 4. The identity of peak 6 is likely a product containing phosphorous based on its retention time. It has an m/z peak of 281, which is greater than that of triphenylphosphine, so it is slightly more massive. Its abundance in the sample was extremely low, as noted by comparing to the CO_2 peak at m/z = 44 in Figure 64 on page 91.

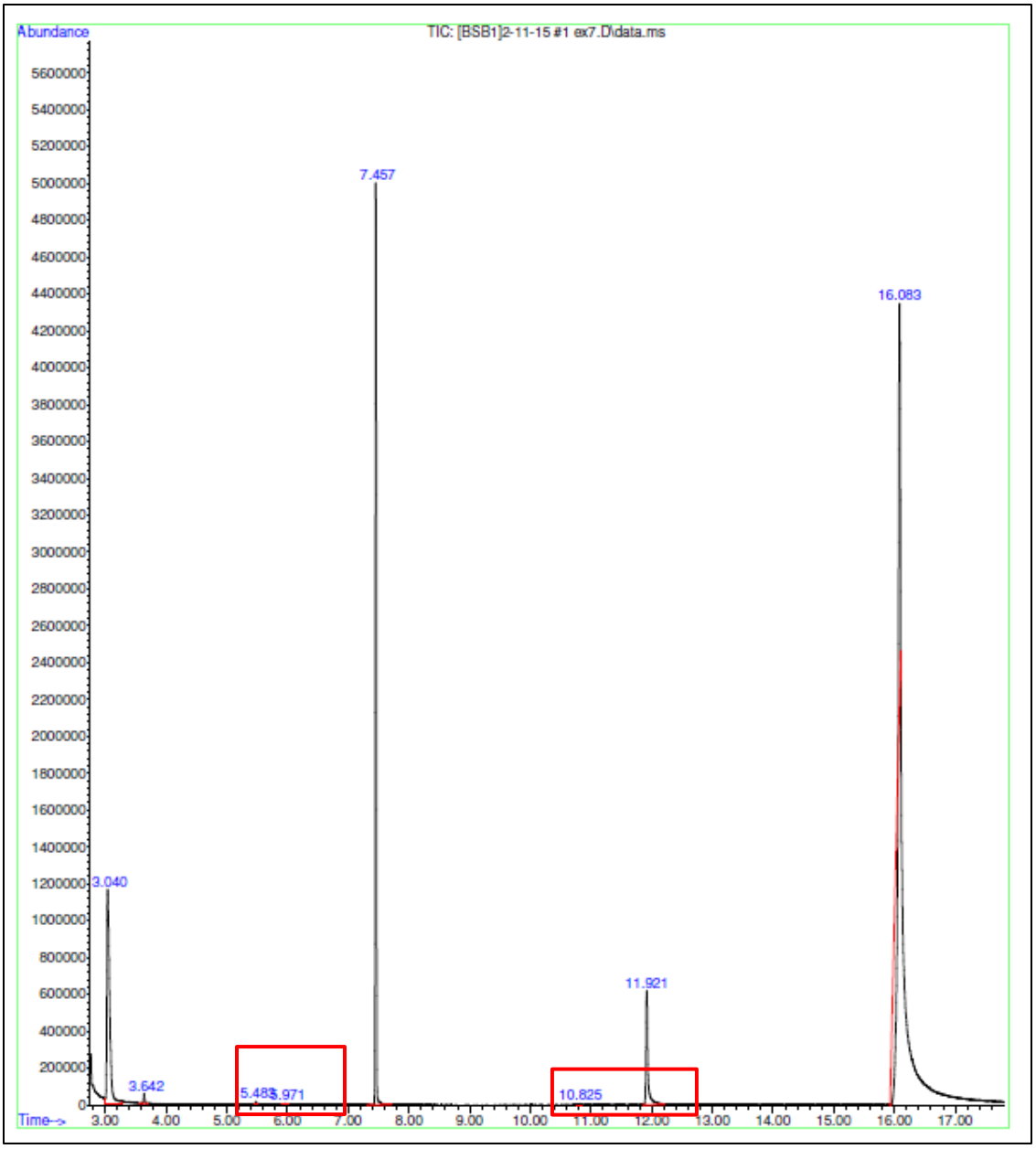


Figure 20. TIC for the reaction. See Figure 21 and Figure 22 for zoomed views of the regions marked with red boxes. The phosphonium salts' retention times were approximately 16 minutes, and they were not resolved well by the instrument.

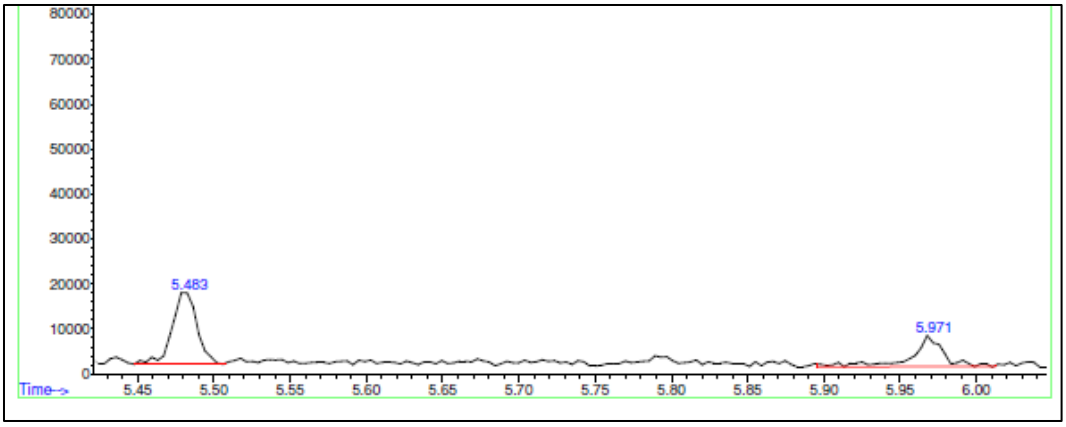


Figure 21. Zoom region 1.

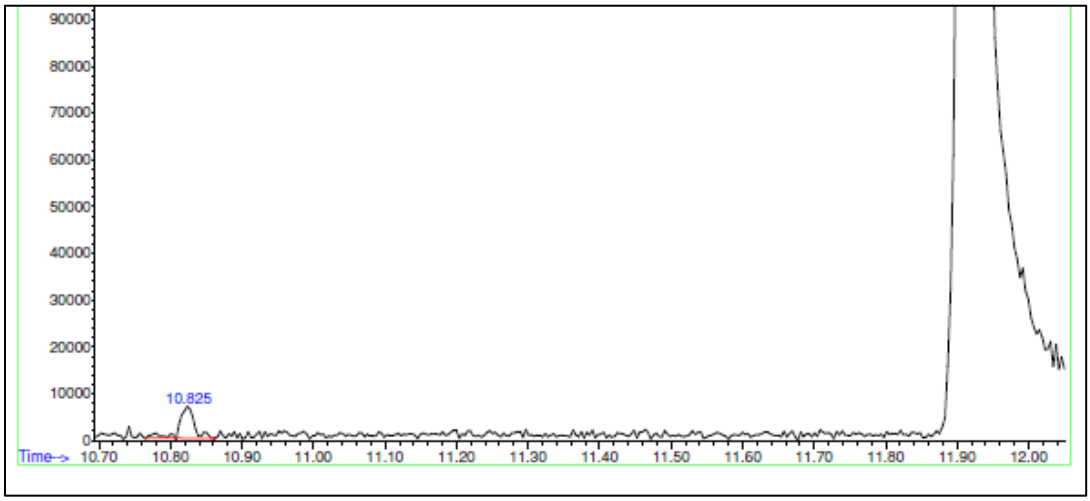


Figure 22. Zoom region 2.

Products produced by Scheme 4 are shown in Figure 23 below. Peaks from the TIC are tabulated in Table 7. See Figure 24 on page 38 for the TIC.

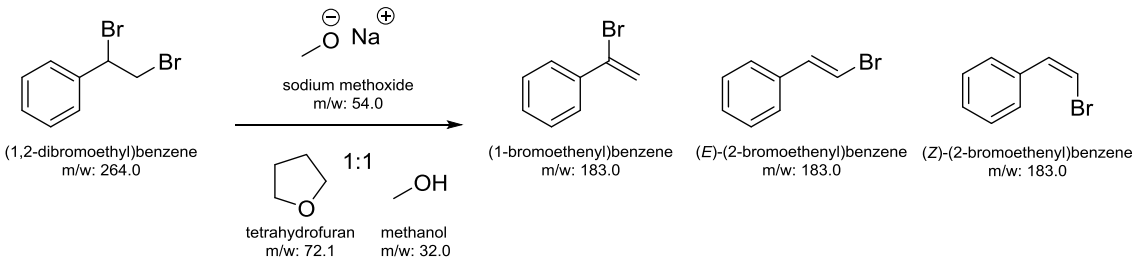


Figure 23. No ether products were characterized by the instrument.

Table 7. GC peaks for Scheme 4. Peaks that were not positively identified are denoted with an asteisk in the identity column.

Peak	Identity	t_R (min)	% comp
1	tetrahydro-2-furanol	3.048	20.37
2	styrene	3.644	0.39
3	butyrolactone	3.719	6.67
4	unknown*	3.750	24.14
5	(1-bromoethenyl)benzene	5.482	35.47
6	(2-bromoethenyl)benzene	5.968	1.71
7	(1,2-dibromoethyl)benzene	7.457	14.26

Peak 1 in Table 7 also appeared in Scheme 3. This peak can be attributed to tetrahydro-2-furanol. Peak 3 is butyrolactone, another derivative of THF. The difference in retention time for peaks 3 and 4 indicates they may be similar, so peak 4 could be another derivative of THF. The mass spectra and reference spectra are contained in Figure 68 – Figure 80 starting on page 96. The temperature of this reaction may have shifted the product distribution toward elimination products, which would at least partially explain the lack of substitution products. Additional experiments would be necessary to test this

theory. A larger alkoxide nucleophile, such as ethoxide, may result in the formation of ether products. Reaction conditions may need to be further optimized for ether products to form. The largest contributor to the lack of ether products may be the solvent mixture used. Methoxide was likely solvated by methanol. This phenomena is known to reduce the nucleophilicity (*21*), which would then essentially limit products formed by methoxide acting as a base. A method to avoid this problem would be to use a nucleophile-solvent pair that is not polar protic, such as an amine.

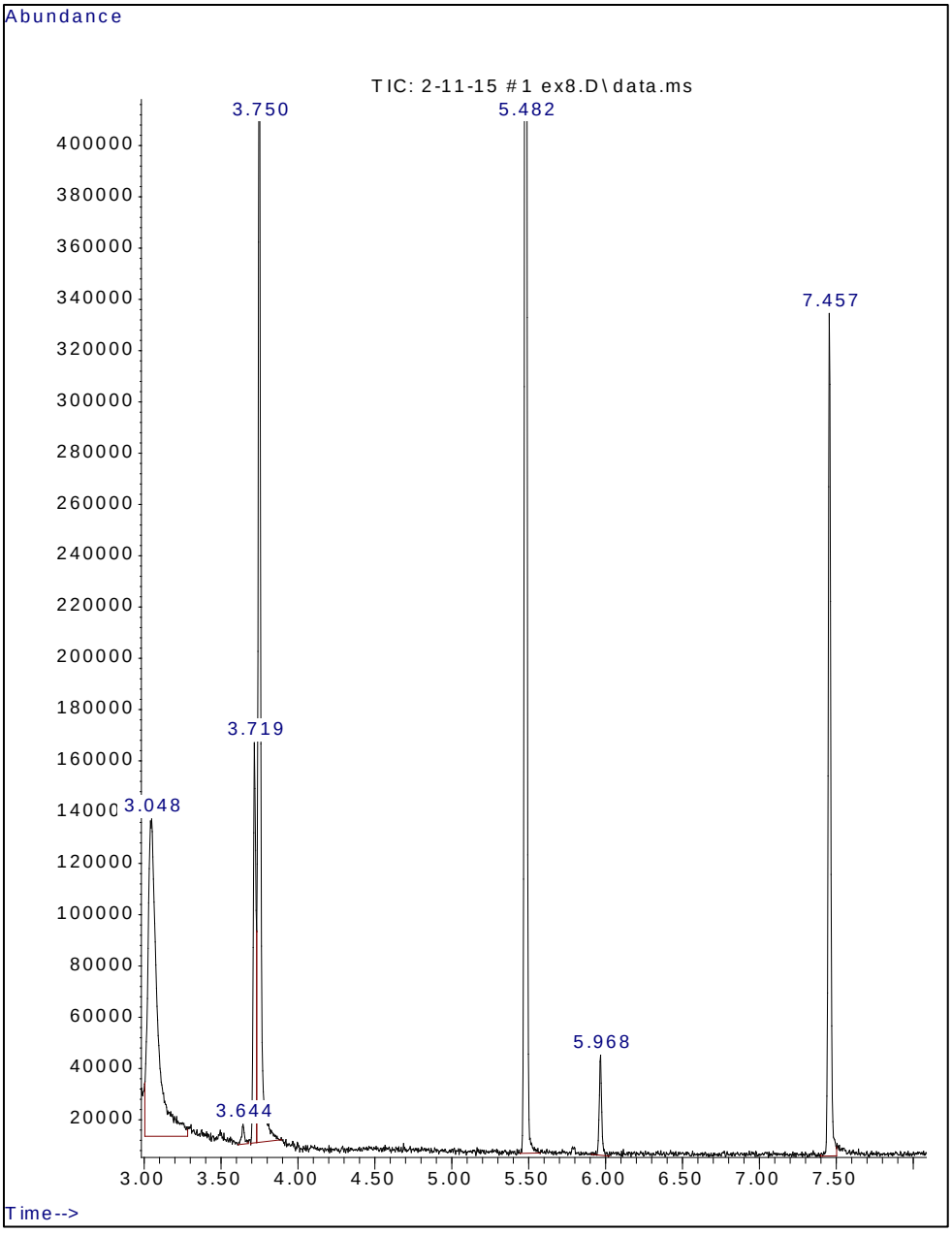


Figure 24. TIC for Scheme 4. Several peaks on this chromatogram are derivatives of THF.

4.2 Student Comprehension Experiment

Student's scores on the pre-quiz and post-quiz were matched and normalized by dividing by four, so that a score of zero corresponded to a completely incorrect quiz, and a score of 1 corresponded to a completely correct quiz. The pre-quiz score was then subtracted from the post-quiz score for each student. Data is included in Table 9, found in Appendix B: Data and Reference Spectra. Aggregate data is included in Table 8 below.

Table 8. Aggregate data from students' scores by class on the quizzes is shown. TA is indicated by a letter. Version was assigned to classes randomly. Totals are shown at the bottom of the table.

Class	TA	Day	Time	Version	Students	Average pre-score	Average post-score	Average score change
1	A	Tu	17:30	1	10	0.700	0.713	0.013
2	B	Tu	8:00	3	18	0.604	0.701	0.097
3	C	F	13:30	1	16	0.453	0.640	0.187
4	D	F	13:30	3	16	0.773	0.706	-0.067
5	E	Tu	17:30	2	17	0.766	0.727	-0.039
6	F	Tu	13:30	2	16	0.617	0.500	-0.117
7	G	Tu	13:30	1	18	0.694	0.604	-0.090
8	H	W	13:30	2	13	0.788	0.731	-0.057
9	I	Tu	8:00	3	17	0.618	0.551	-0.067
10	J	W	8:00	3	19	0.728	0.625	-0.103
11	B	Th	8:00	2	17	0.642	0.408	-0.234
12	K	Th	8:00	1	18	0.653	0.583	-0.070
13	A	Th	17:30	2	15	0.775	0.767	-0.008
14	F	Th	13:30	3	19	0.632	0.632	0.000
15	L	W	13:30	3	14	0.732	0.786	0.054
16	L	W	17:30	3	18	0.590	0.674	0.084
17	M	W	17:30	1	18	0.590	0.514	-0.076
18	N	F	8:00	1	14	0.652	0.670	0.018
19	J	F	8:00	1	18	0.510	0.646	0.136
20	J	Th	8:00	2	20	0.638	0.563	-0.075
				Totals:	**331**	**0.658**	**0.637**	**-0.021**

The standardized score change was then calculated and tested for normality, as shown in Figure 25. A confidence level of $\alpha = 0.05$ was selected. The null and alternative hypotheses were:

H_0: $\mu_{post\text{-}quiz} - \mu_{pre\text{-}quiz} = 0$

H_1: $\mu_{post\text{-}quiz} - \mu_{pre\text{-}quiz} > 0$

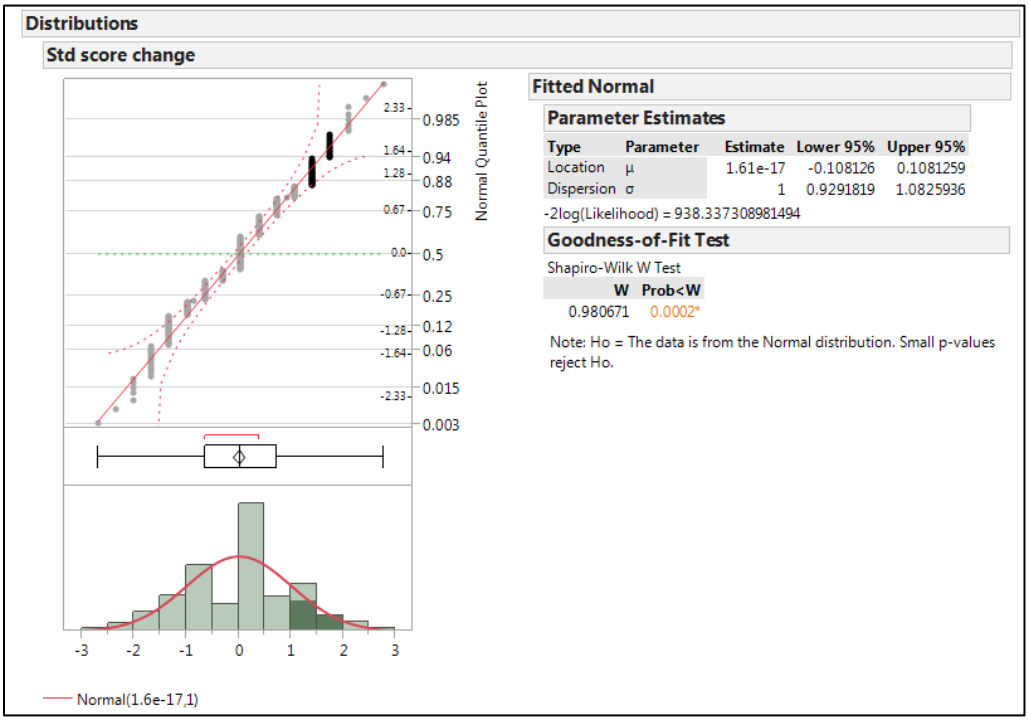


Figure 25. The residuals were not normally distributed, so a parametric test was used to analyze the data.

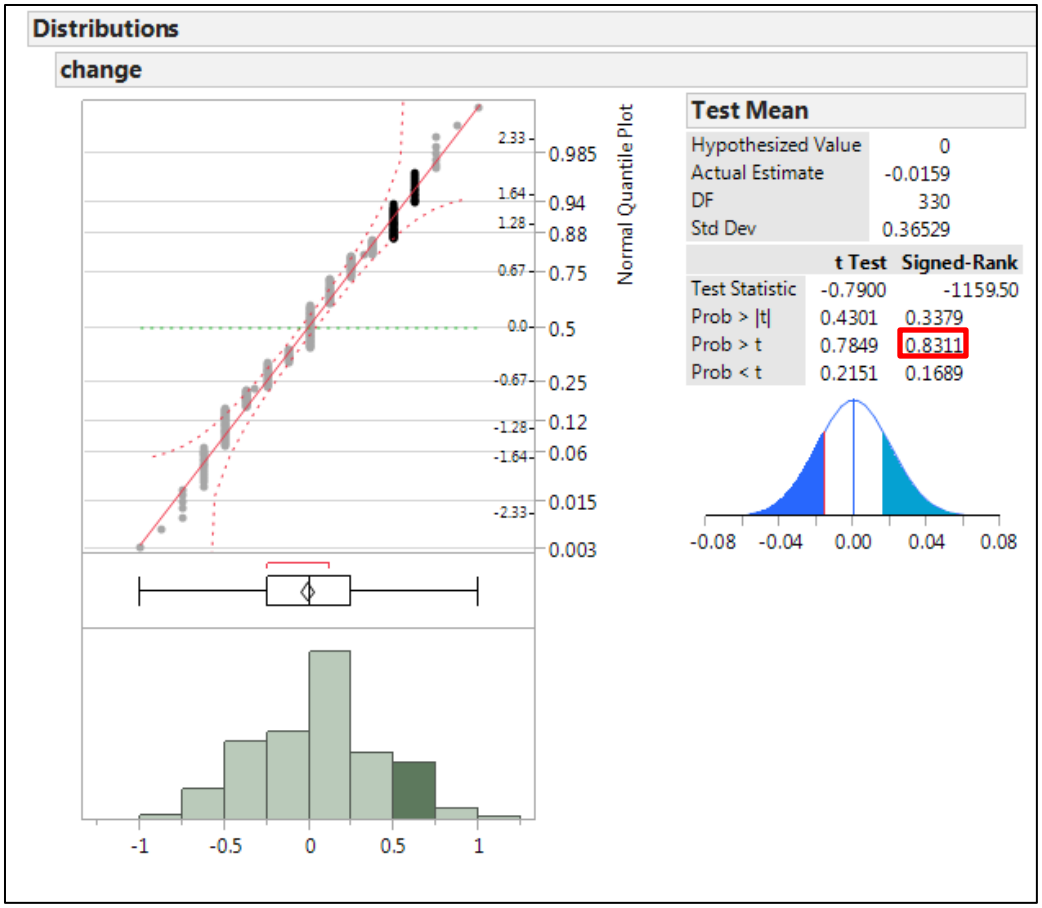


Figure 26. The p-value of interest corresponds to the alternative hypothesis. In this case, the p-value indicates the likelihood of encountering a value greater than the test statistic, so p = 0.8311, which is boxed above in red.

The Wilcoxon Signed Rank test was used to test the null hypothesis, and resulted in a p-value of 0.8311 as shown in Figure 26. Because $p > \alpha$, the null hypothesis was not rejected.

The data may not accurately represent what students knew. For example, students who suggested the temperature was too high for substitution products to be formed on their quizzes received at most 2 out of 4, which did not accurately represent their understanding of the reactions. Furthermore, the subjective nature of assessing the explanation portion of the quizzes likely introduced error into the data. Without explicitly

telling students to identify the mechanism, and explain why that mechanism occurred based on the characteristics of the nucleophile, many students did not include those parts in their answer. An additional source of variability was the amount of time it had been since a student had taken CHEM 2510. The ability of a student to answer the questions correctly likely is influenced by whether he or she learned the material two years previously, the previous semester, or was learning the material concurrently in CHEM 2510. Furthermore, the lack of randomization within each class section may have impacted the results. Unfortunately, an easy method to randomize the order of several hundred quizzes being printed is not a simple feat. Providing student with exposure to the same reaction type on the data sheet, pre-quiz, and discussion, but then quizzing them on a different reaction type on the post-quiz may not have been the ideal method to test whether the activity helped them to understand the material, even though they were provided with background material that described the reaction types and mechanisms at the beginning of the activity. Modifications to the activity materials likely must be considered.

Chapter 5: Conclusions

Unexpected products observed in reactions demonstrate how related mechanistic pathways are relevant to an understanding of substitution and elimination chemistry. This supports the use of (1,2-dibromoethyl)benzene as a suitable substrate for use in a teaching laboratory. Overall, product characterization was simple enough that students could likely identify products themselves if provided with spectra from their product samples. However, some minor changes to the experimental procedures may need to be considered before implementing the reactions as a new lab experiment.

The activity did not improve students' performance on the quiz. Based on the structure of the activity, changes can likely be made that will improve the activity for the students, and potentially find significant improvements in student understanding in future experiments.

Chapter 6: Recommendations

One potential source of variance in the reactions conducted is the different size of the glassware filled with armor beads for the four reaction setup shown in Figure 7. This may cause differences in heating between reactions. This would not be a problem if students were to carry out these reactions because they each have a standardized set of glassware to use. Several relatively easy improvements can be made to the experimental procedures that will make identifying reaction products easier, and may also yield a greater variety of products than current methods. For Scheme 3 and Scheme 4, using inhibited THF may decrease the occurrence of its derivatives in product samples, particularly as the derivatives observed are oxidized versions of THF. At a minimum, the source of these derivatives should be identified, as these products could potentially oxidize to a peroxide, which would add a significant hazard to these experiments. Two likely possibilities are the THF used in these experiments was beginning to expire, and was oxidizing in air which diffused into the solvent vessel, or THF is being oxidized by unknown mechanisms while the experiments are being conducted. One method to test which of these is the source of oxidized THF might be to simultaneously run reactions using newly purchased THF and an older supply, and compare the resulting chromatograms. If there is no difference, then it is more likely THF is being oxidized during the experiments. Testing one or two other nucleophiles that are good nucleophiles but weak bases, such as azide salt or an amine, may yield S_N2 products which can be completely characterized. Testing at multiple temperatures may allow for characterization of the shift between

substitution and elimination products in these reactions, and implementing that component in the teaching laboratory may give students a better idea of what constitutes a high temperature that will only produce elimination products. As many students indicated on their quizzes, the temperature of 50 °C may have been too high for ether products to form in Scheme 4. To further explore the design space, lower temperatures and an ethoxide nucleophile should be used in a modified Scheme 4.

To fully implement the learning objectives outlined in

Combining the three versions of the discussion activity into one and adding an S_N2 only reaction would likely increase the efficacy of the activity by walking students through an appropriate methodology to identify each reaction type. This would essentially expand the amount of time each student spends practicing identifying the reactions. Additionally, a question should be added to either the pre or post-quiz that asks students when they took CHEM 2510, as blocking on this variable may be helpful in discovering a significant result. Randomly pairing the quiz versions would be beneficial to reducing error from nuisance variables.

The structure of the explanation question on the quizzes should be changed to better characterize what students know about each relevant reaction parameter. The changes should explicitly ask students to state which mechanism(s) occurred, and which products they formed. Then, ask the students what properties of the nucleophile in the reaction influenced the mechanisms which occurred with regard to the ability of the nucleophile to act as a nucleophile and as a base. Additionally, the explanation should ask whether the connectivity of the substrate has an effect on which mechanisms can occur. This would identify whether students are familiar with the antiperiplanarity requirement for E2

reactions. Finally, the explanation question should ask whether any other factors of the reaction conditions contribute to the mechanisms that occurred. This will test whether students can identify that elimination will occur in greater proportion with increasing temperature. Overall, these changes will make the activity a more robust assessment tool.

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Appendix A: Documents for Lab Experiment

TA Instructions for S_N/E Activity - UPDATE

CHEM 2540 – SP15

Today in Laboratory, your students will have the opportunity to participate in an educational study. Students can earn up to ten (10) points of extra credit by working in groups to analyze data and answer discussion questions pertaining to a specific substitution/elimination reaction. The study includes a quiz before and after the discussion activity, and students will have the choice to opt out of the study and still earn extra credit for their discussion.

Activity Timeline UPDATE

Prior to the Start of Class: Make sure you have the following items appropriate for your section. These items will be placed in your TA mailbox in CE 431.

1. **NEW** Consent to Participate in Research Form (stapled handout) – one per student
2. **NEW** S_N/E Activity Pre-Quiz – Five (5) minutes – one per student
3. Introduction to S_N/E Activity – one per student
4. S_N/E Activity Discussion Questions – Fifteen (15) minutes – only one collected per group
5. S_N/E Activity Data Set – one per student
6. **NEW** S_N/E Activity Post-Quiz - Five (5) minutes – one per student

Start of Class Announcement: Along with your other announcements at the beginning of class, announce that there will be an extra credit opportunity after the Aspirin Experiment has concluded for the day.

Prior to Activity: Make sure everyone's lab work has finished and the laboratory space and equipment is clean and tidy. The activity can be started as soon as everyone has completed his or her lab work for the day. However, the activity should be started no later than 11:20 am, 4:20 pm, or 8:50 pm.

Begin Activity: Read the Recruitment Script by Dr. Clark (on the back of this page)

Distribute Consent to Participate in Research Form: Instruct EACH STUDENT to read the packet, detach the last page from the packet, and sign this copy of the consent if they wish to participate. The rest of the Consent packet is theirs to keep. Collect the signed Consent Forms from your students and put them away. Example of signed consent form attached.

Pre-Quiz (5 minutes): Pass out one copy of the Pre-Quiz to each student. Instruct your students to write their name on the quiz, and instruct them to answer the questions individually. Students should not talk to each other during the quiz. Give your class five (5) min to complete it. Collect all of the Pre-Quizzes and put them away.

Discussion and Data Analysis (15 minutes): Organize the class into groups of 3, 4, or 5 students and then pass out the Introduction, Discussion Questions, and Data Set. Have students work together to answer the questions. When the time limit is reached, collect the Discussion form (one per group) and make sure all students' names are on the Discussion Questions that are turned in.

Post-Quiz (5 minutes): Pass out one copy of the Post-Quiz to each student. Instruct your students to write their name on the quiz, and instruct them to answer the questions individually. Students should not talk to each other during the quiz. Give your class five (5) min to complete it. Collect all of the Post-Quizzes. That is the end of the activity.

Make sure the Consent Forms, Pre-Quiz, Discussion, Post-Quiz, and are all present and neatly ordered and place them in your TA Mailbox in CE 431.

Thanks so much for your help with this activity! -NMP

Figure 27. Instructions given to teaching assistants administering the experiment.

S_NE Activity – Data Set

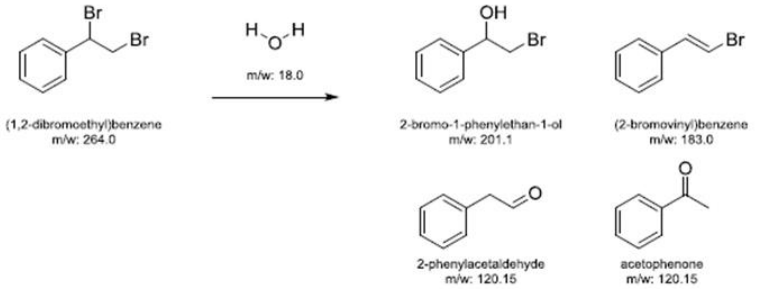


Table 1: Reagent table for reaction 2.

T = 50°C Reaction duration: 60 min	Reagent	Mass (g)	MW	mmol	ε
	(1,2-dibromoethyl)benzene	0.1105	263.96	0.4186	1
	water	10	18.02		excess

Table 2: GC peaks for reaction 2.

Peak	Identity	t_R (min)	% comp
1	benzeneacetaldehyde	4.666	0.40
2	acetophenone	4.828	1.08
3	(2-bromoethenyl)benzene	5.971	0.27
4	α-(bromomethyl)-benezenemethanol	6.924	3.58
5	(1,2-dibromoethyl)benzene	7.457	94.66

Figure 28. Data set given to students with version 2. This data set pertains to the solvolysis reaction.

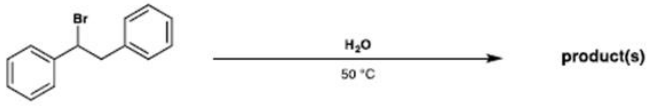
S_NE Activity - Pre-Quiz

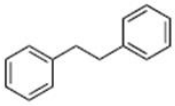
CHEM 2540 – SP15

Print Your Name Here *OSU.number*

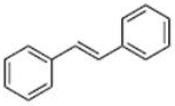
Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

1. **Predict the Product.** Select the product outcome (Letters A-E) for the reaction shown:

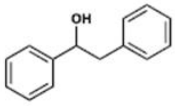




(A)



(B)



(C)

both **(A)** and **(B)**

(D)

both **(B)** and **(C)**

(E)

2. **Explain Your Choice.** Given the conditions above, explain your product selection.

Pre2

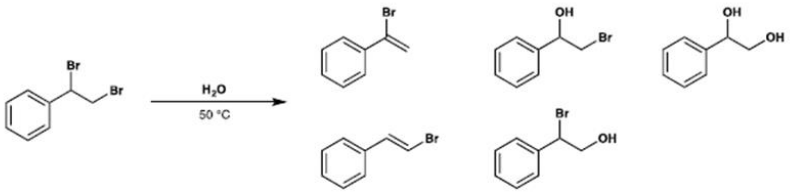
Figure 29. Pre-quiz given to students with version 2. This pre-quiz tested understanding of solvolysis.

S_N/E Activity – Discussion Questions

CHEM 2540 – SP15

Your Names *Your Section* *Your Lab/TA*

Learning Objective: Use reaction data to answer questions about S_N/E chemical transformations.



1. Using the data table for the reaction shown, can you determine which of the proposed products above were actually observed? Circle those structures. Were there any products formed that were not listed above? If so, draw the structure(s) above to the right.

2. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a good or bad nucleophile? Explain your reasoning.

3. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a strong or weak base? Explain your reasoning.

4. Can you determine the mechanism(s) that occurred to yield the observed products of the reaction? For each mechanism listed, explain how you determined it did or did not occur.

   S_N2:

   S_N1:

   E2:

   E1:

5. What explains the identity of the major component of this reaction mixture?

D2

Figure 30. Discussion activity for version 2. This activity also pertained to solvolysis.

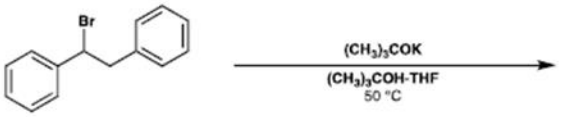
S_NE Activity - Post-Quiz

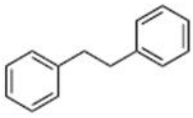
CHEM 2540 – SP15

Print Your Name Here *OSU.number*

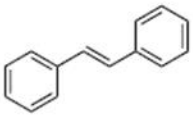
Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

1. **Predict the Product.** Select the product outcome (Letters A-E) for the reaction shown:

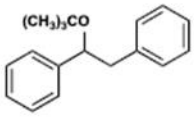




(A)



(B)



(C)

(D) both (A) and (B)

(E) both (B) and (C)

2. **Explain Your Choice.** Given the conditions above, explain your product selection.

Figure 31. Post-quiz for version 2. The quiz tested knowledge of the E2 mechanism.

S_NE Activity – Data Set

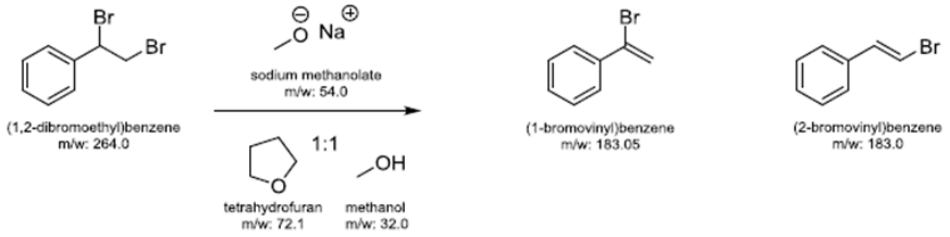


Table 1: Reagent table for reaction 4.

	Reagent	Mass (g)	MW	mmol	ε
T = 50°C Reaction duration: 53 min 10 mL solvent	(1,2-dibromoethyl)benzene	0.1065	263.96	0.403	1
	Sodium methoxide	0.0876	54	1.622	4.02
	Solvent: 1:1 THF:methanol				

Table 2: GC peaks for reaction 4.

Peak	Identity	t_R (min)	% comp
1	(1-bromoethenyl)benzene	5.482	68.95
2	(2-bromoethenyl)benzene	5.968	3.32
3	(1,2-dibromoethyl)benzene	7.458	27.72

Figure 32. Data set 3 was the S_N2 and E2 reaction.

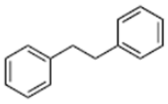
S_NE Activity - Pre-Quiz

CHEM 2540 – SP15

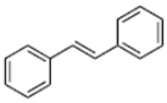
Print Your Name Here *OSU.number*

Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

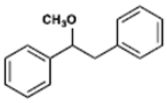
1. **Predict the Product.** Select the product outcome (Letters A-E) for the reaction shown:



(A)



(B)



(C)

both **(A)** and **(B)**

(D)

both **(B)** and **(C)**

(E)

2. **Explain Your Choice.** Given the conditions above, explain your product selection.

Pre3

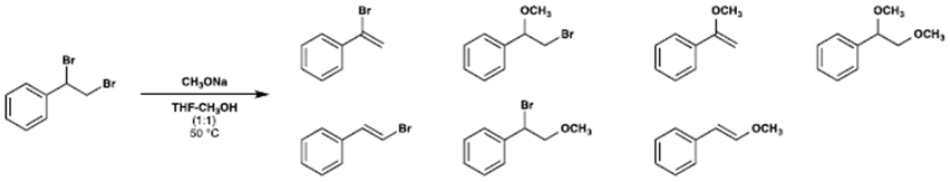
Figure 33. Pre-quiz 3 tested students' knowledge of reactions with a good nucleophile and strong base.

S_N/E Activity – Discussion Questions

CHEM 2540 – SP15

Your Names *Your Section* *Your Lab/TA*

Learning Objective: Use reaction data to answer questions about S_N/E chemical transformations.



1. Using the data table for the reaction shown, can you determine which of the proposed products above were actually observed? Circle those structures. Were there any products formed that were not listed above? If so, draw the structure(s) above to the right.

2. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a good or bad nucleophile? Explain your reasoning.

3. Based on the actual products that were formed, can you determine if the nucleophile/base used in the reaction above is a strong or weak base? Explain your reasoning.

4. Can you determine the mechanism(s) that occurred to yield the observed products of the reaction? For each mechanism listed, explain how you determined it did or did not occur.

   S_N2:

   S_N1:

   E2:

   E1:

5. What explains the identity of the major component of this reaction mixture?

D3

Figure 34. The discussion activity for version 3 explored students' knowledge of reactions with a good nucleophile and strong base.

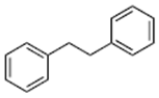
S_NE Activity - Post-Quiz

CHEM 2540 – SP15

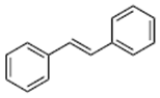
Print Your Name Here *OSU.number*

Learning Objective: Identify the products of a S_N/E chemical transformation based on analysis of the reaction parameters (reagents, equivalents, solvents, temperature, etc.).

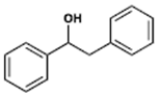
1. **Predict the Product.** Select the product outcome (Letters A-E) for the reaction shown:



(A)



(B)



(C)

both **(A)** and **(B)**

(D)

both **(B)** and **(C)**

(E)

2. **Explain Your Choice.** Given the conditions above, explain your product selection.

Post3A

Figure 35. Post-quiz 3 tested students' understanding of solvolysis.

Appendix B: Data and Reference Spectra

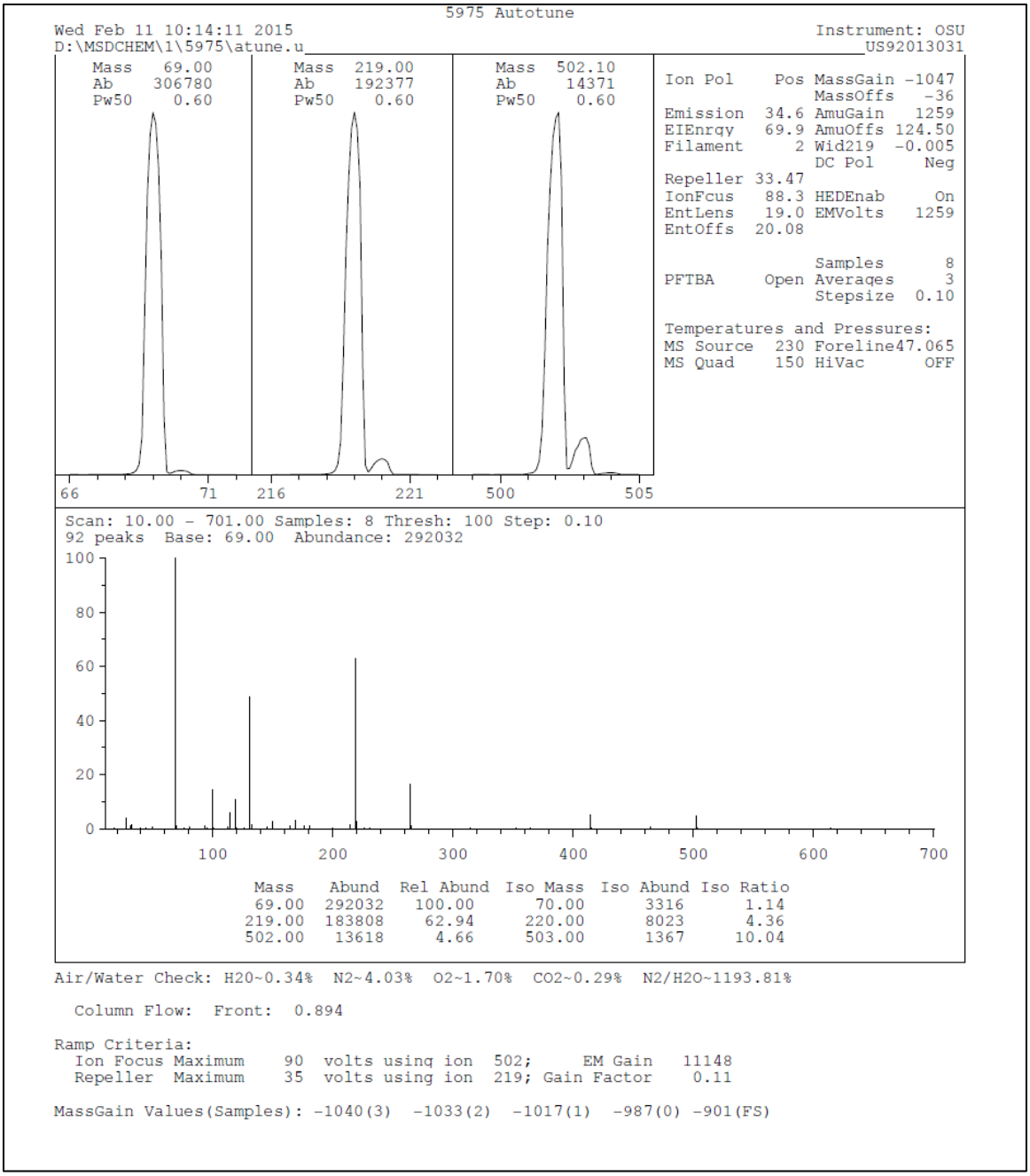


Figure 36. Mass spectrometer tune file.

Report 1. Area Percent Report for Scheme 1.

Area Percent Report

Data Path : D:\msdchem\1\DATA\Jonathan Ruffley\
Data File : 2-11-15 #1 ex5.D
Acq On : 11 Feb 2015 10:26
Operator : JPR
Sample : 1 #5
Misc :
ALS Vial : 19 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : D:\msdchem\1\METHODS\UGO-30min.M
Title :

Signal : TIC: 2-11-15 #1 ex5.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.546	236	247	257	BV	583410	5844606	14.97%	12.475%
2	5.486	735	747	762	BB	3765182	39054891	100.00%	83.360%
3	5.970	860	872	881	BB	186672	1951448	5.00%	4.165%

Sum of corrected areas: 46850945

UGO-30min.M Wed Feb 11 22:23:14 2015

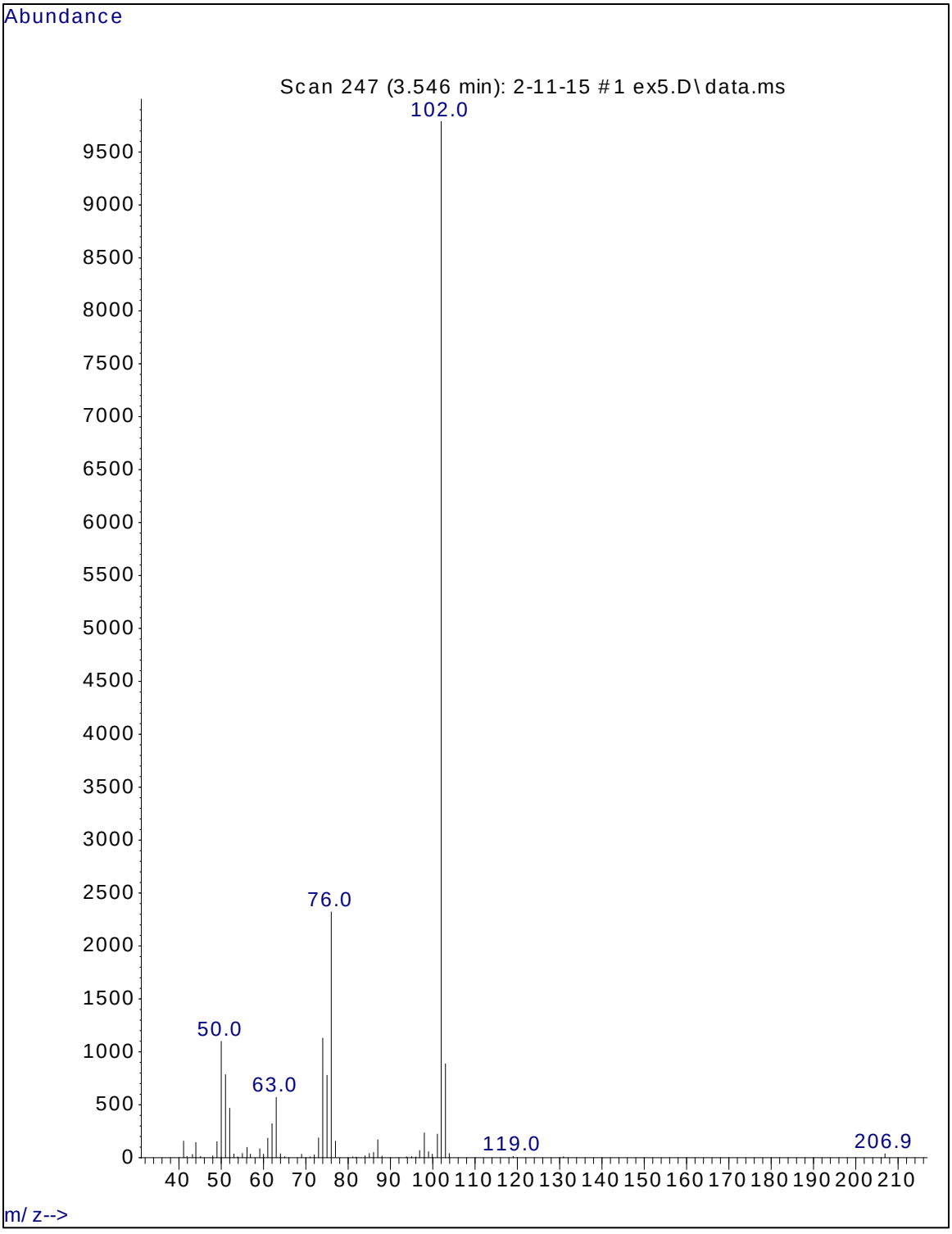


Figure 37. Mass spectrum for peak 1, Scheme 1. The reference spectrum is shown in Figure 38 on page 63.

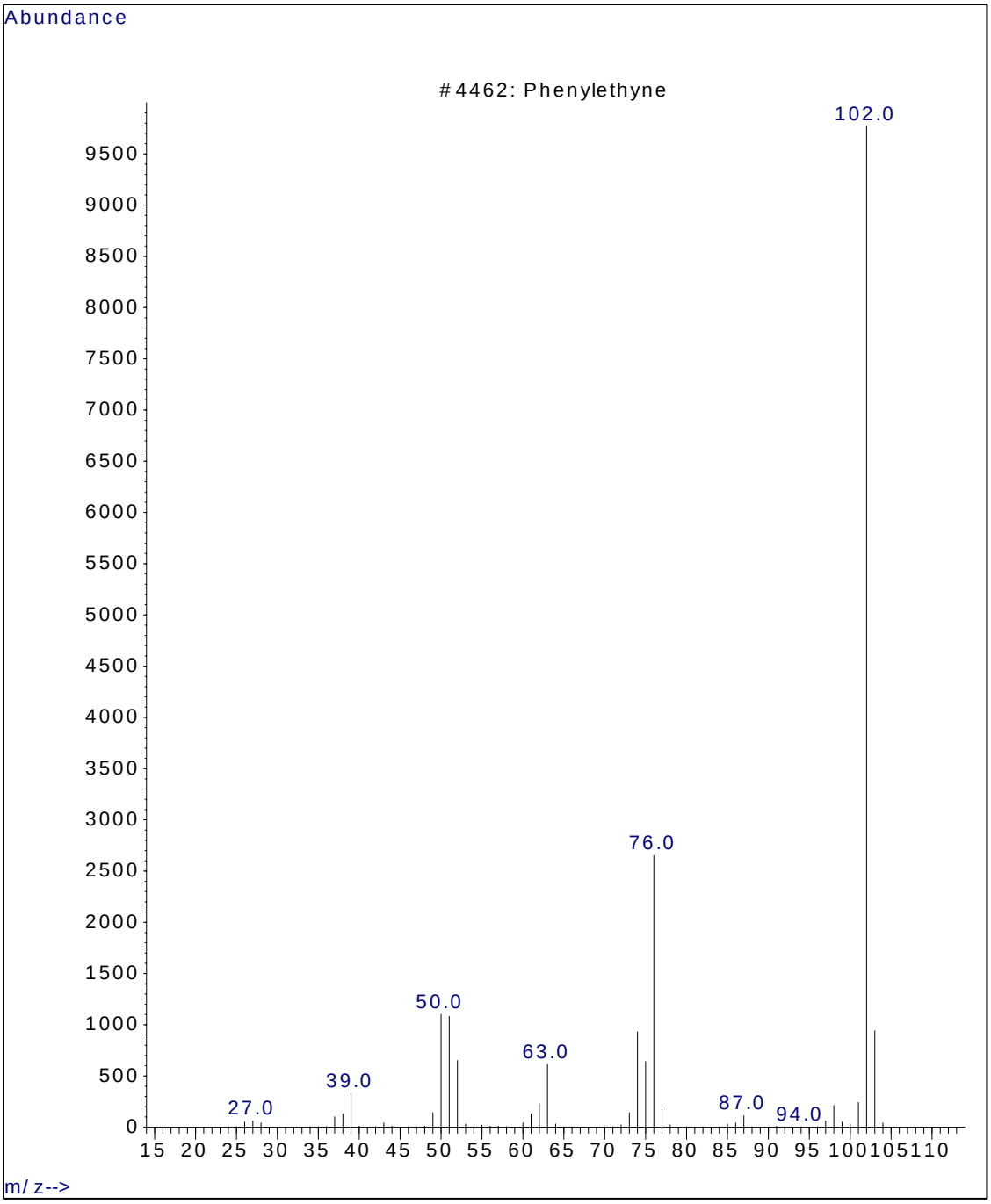


Figure 38. The identity of peak 1, Scheme 1 is phenyethylene. This compound is also commonly known as ethynylbenzene.

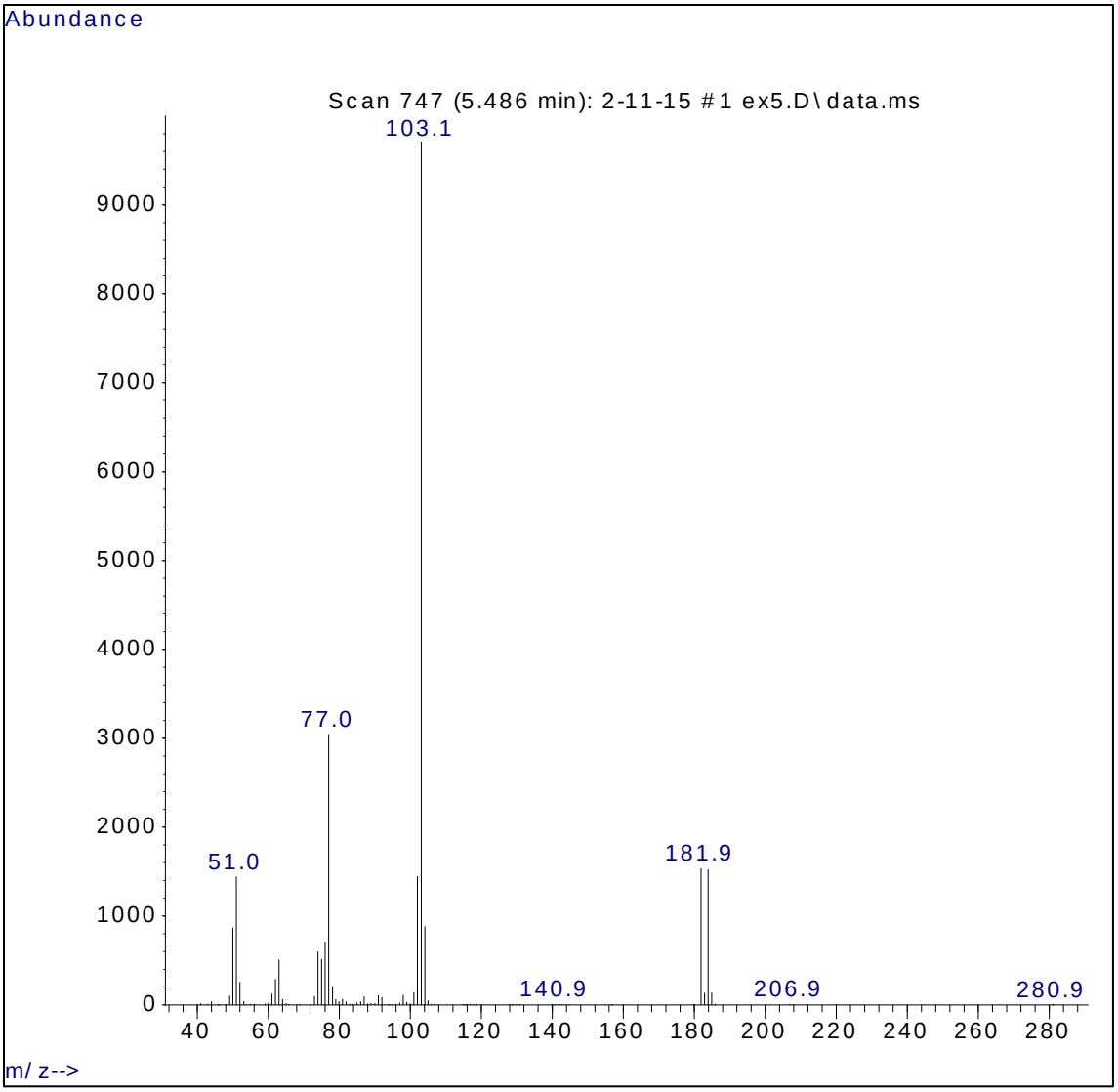


Figure 39. Mass spectrum for peak 2, Scheme 1. The reference spectrum is shown in Figure 40 on page 65.

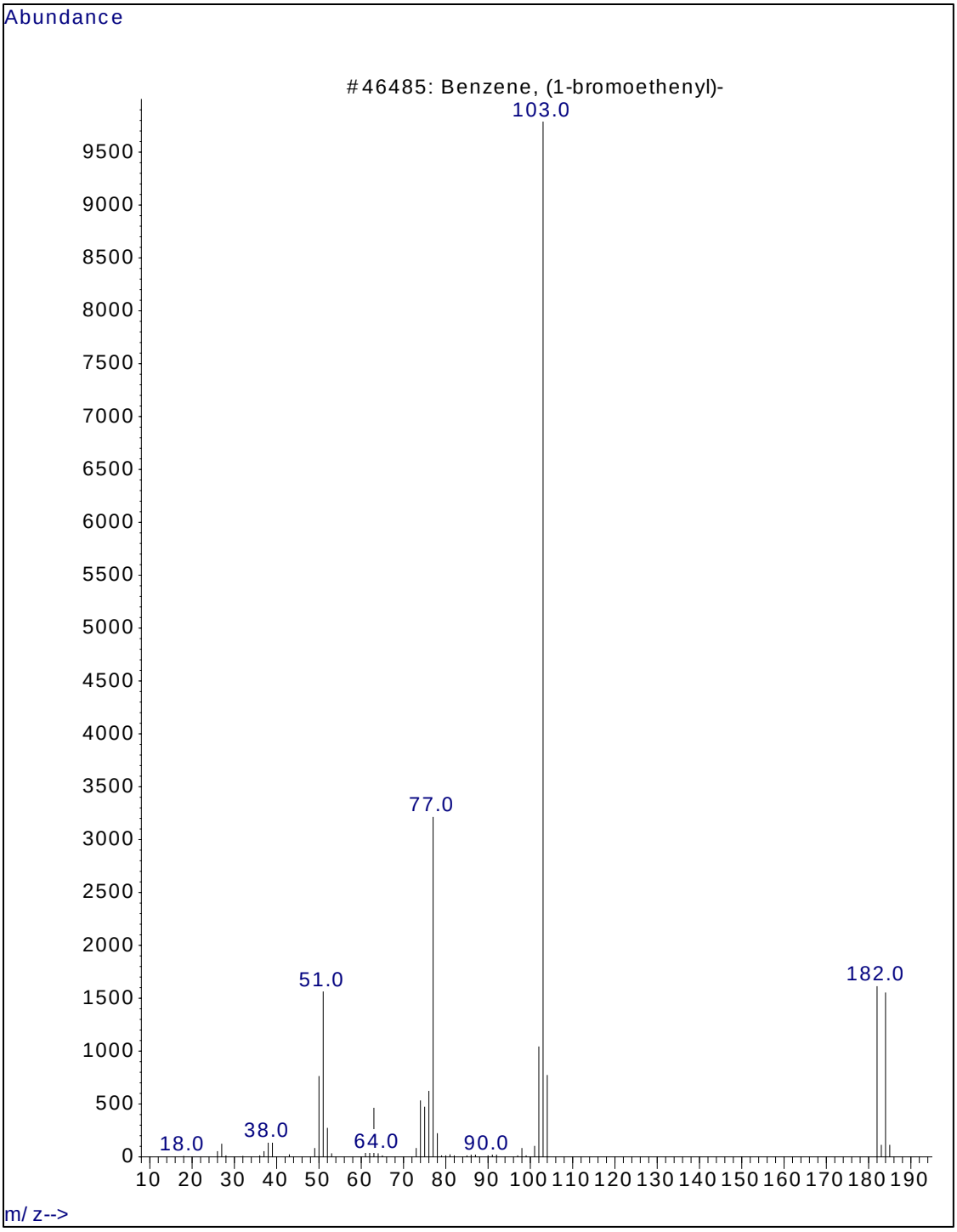


Figure 40. The identity of peak 2, Scheme 1 is (1-bromoethenyl)benzene. This compound is also known as (1-bromovinyl)benzene.

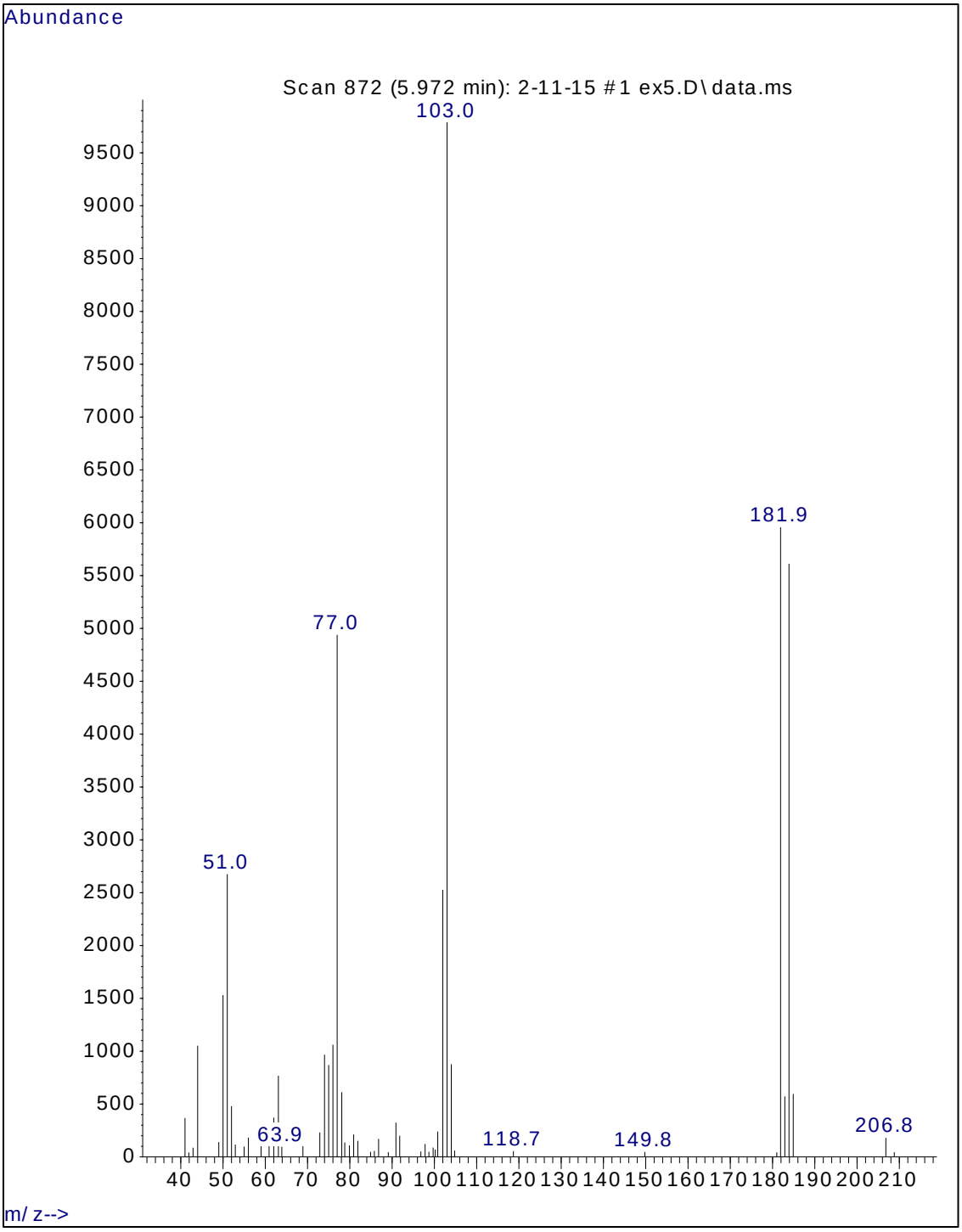


Figure 41. Mass spectrum for peak 3, Scheme 1. The reference spectrum is shown in Figure 42 on page 67.

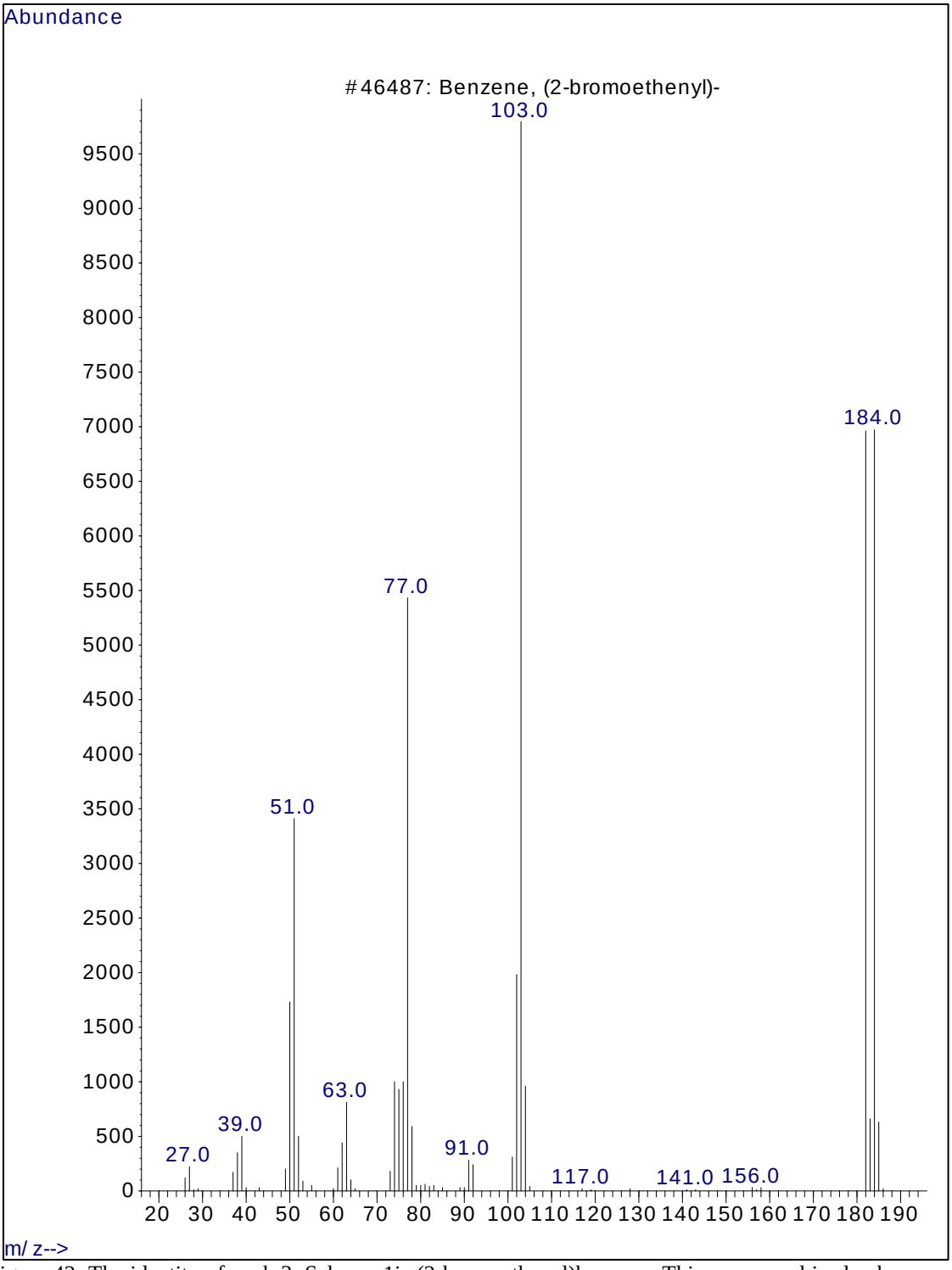


Figure 42. The identity of peak 3, Scheme 1is (2-bromoethenyl)benzene. This compound is also known as (2-bromovinyl)benzene.

Report 2. Area Percent Report for Scheme 2.

Area Percent Report

Data Path : D:\msdchem\1\DATA\Jonathan Ruffley\
Data File : 2-11-15 #1 ex6.D
Acq On : 11 Feb 2015 11:01
Operator : JPR
Sample : 1 #6
Misc :
ALS Vial : 20 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : D:\msdchem\1\METHODS\UGO-30min.M
Title :

Signal : TIC: 2-11-15 #1 ex6.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.640	266	271	279	PV	48094	483521	2.27%	2.067%
2	4.666	510	536	543	VV 4	3900	90873	0.43%	0.389%
3	4.828	568	577	594	PV 4	15756	243489	1.14%	1.041%
4	5.971	866	872	879	VV 2	5141	60564	0.28%	0.259%
5	6.877	1088	1105	1110	PV 5	4675	56483	0.27%	0.242%
6	6.924	1110	1117	1155	VV 2	51164	806358	3.78%	3.448%
7	7.457	1238	1255	1266	PBA	2028268	21314277	100.00%	91.137%
8	7.874	1354	1362	1379	PV 3	30944	331616	1.56%	1.418%

Sum of corrected areas: 23387180

UGO-30min.M Wed Mar 04 22:21:00 2015

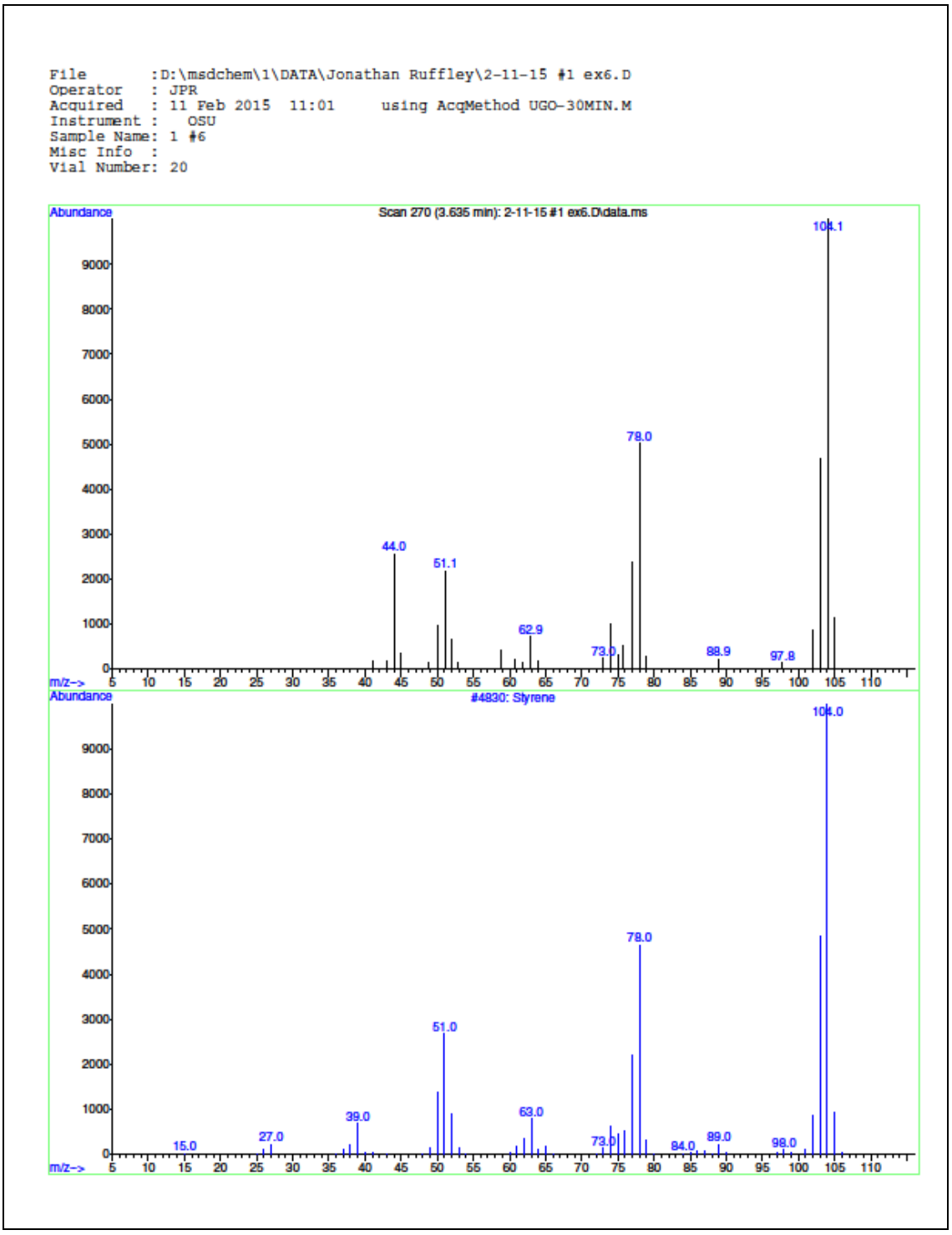


Figure 43. Peak 1, Scheme 2, is styrene. The peak at m/z =44 is an artifact of the presence of CO_2 in the instrument.

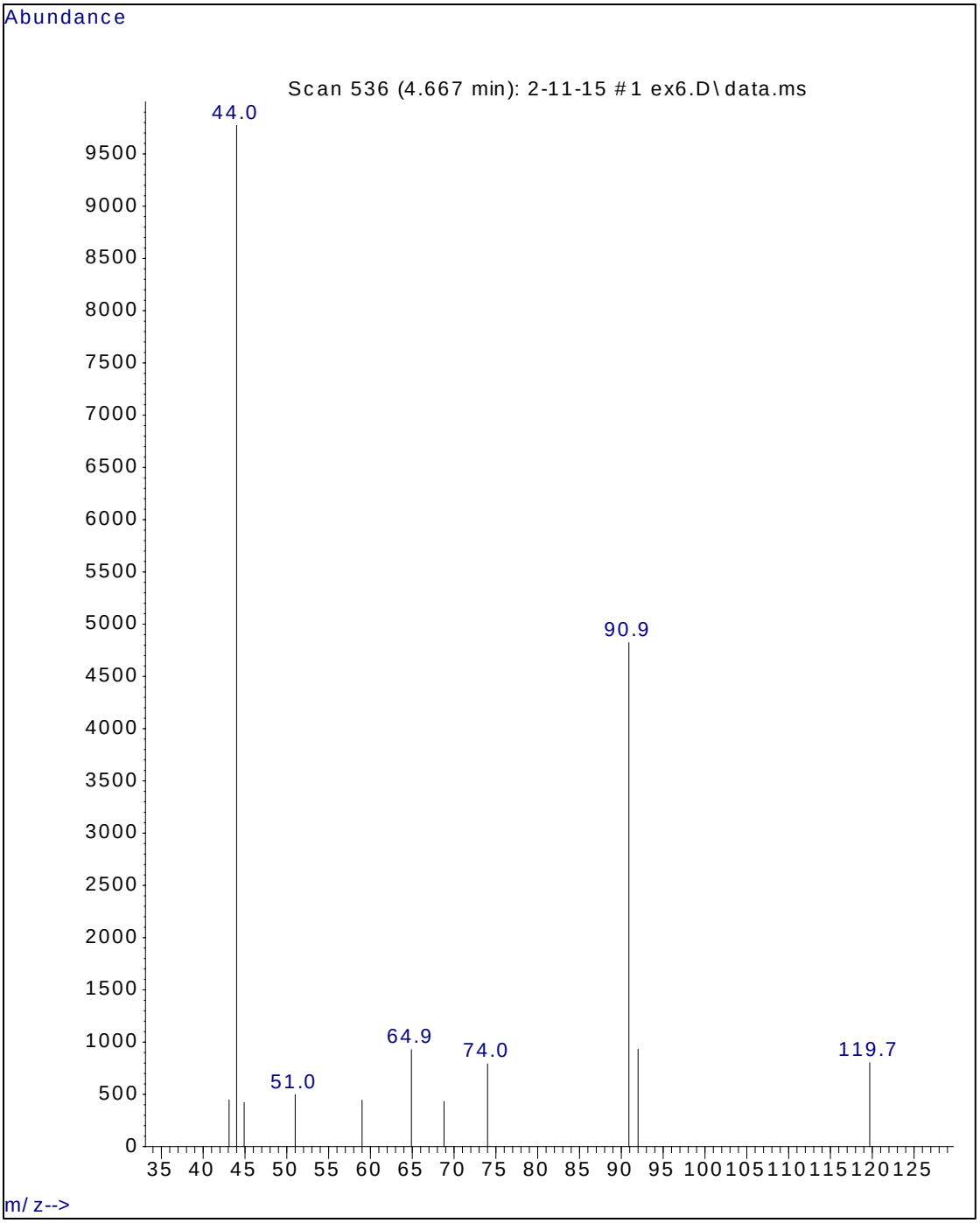


Figure 44. Mass spectrum for peak 2, Scheme 2. The reference spectrum is shown in Figure 45.

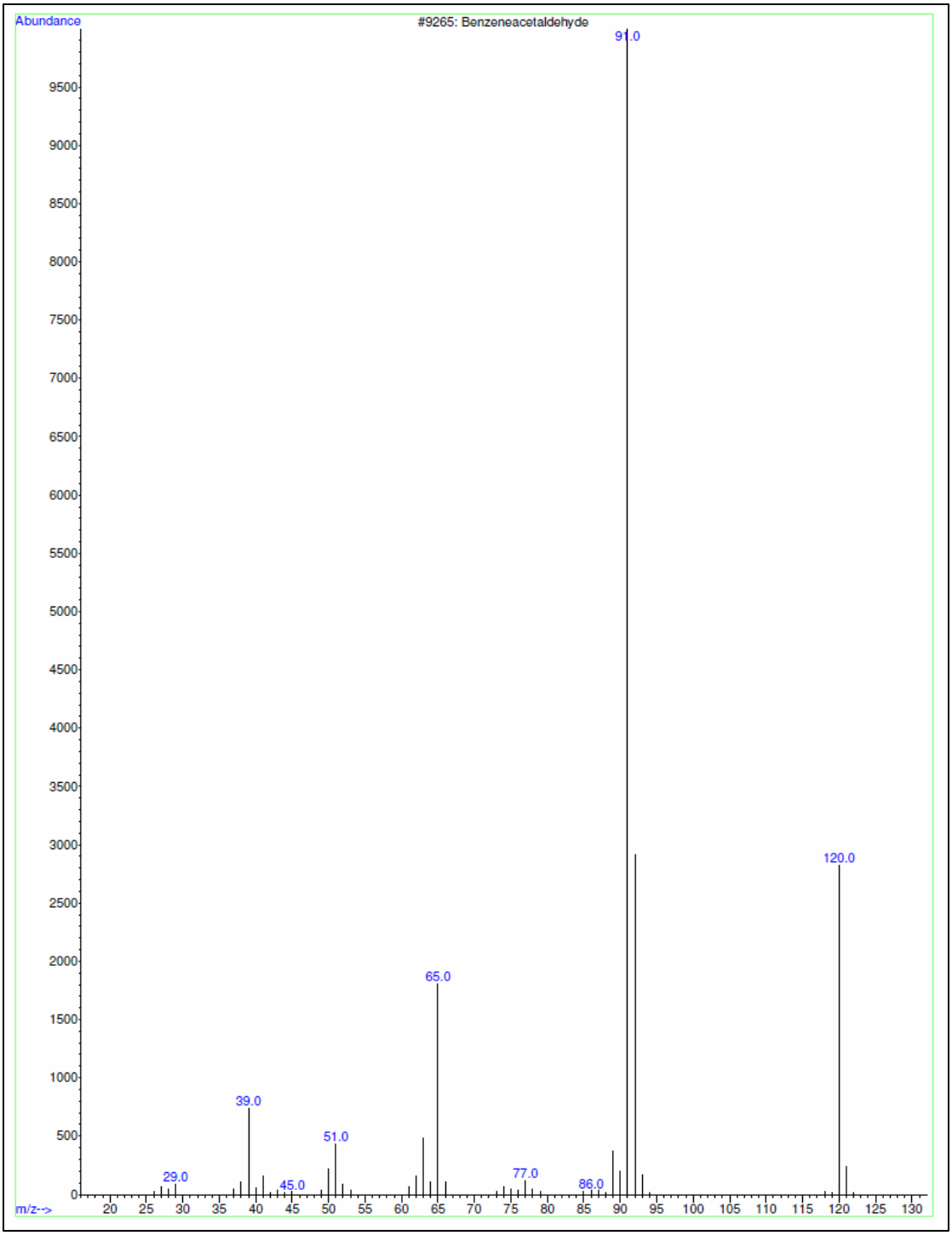


Figure 45. The identity of peak 2, Scheme 2, is benzeneacetaldehyde. This compound is also known as phenylacetaldehyde.

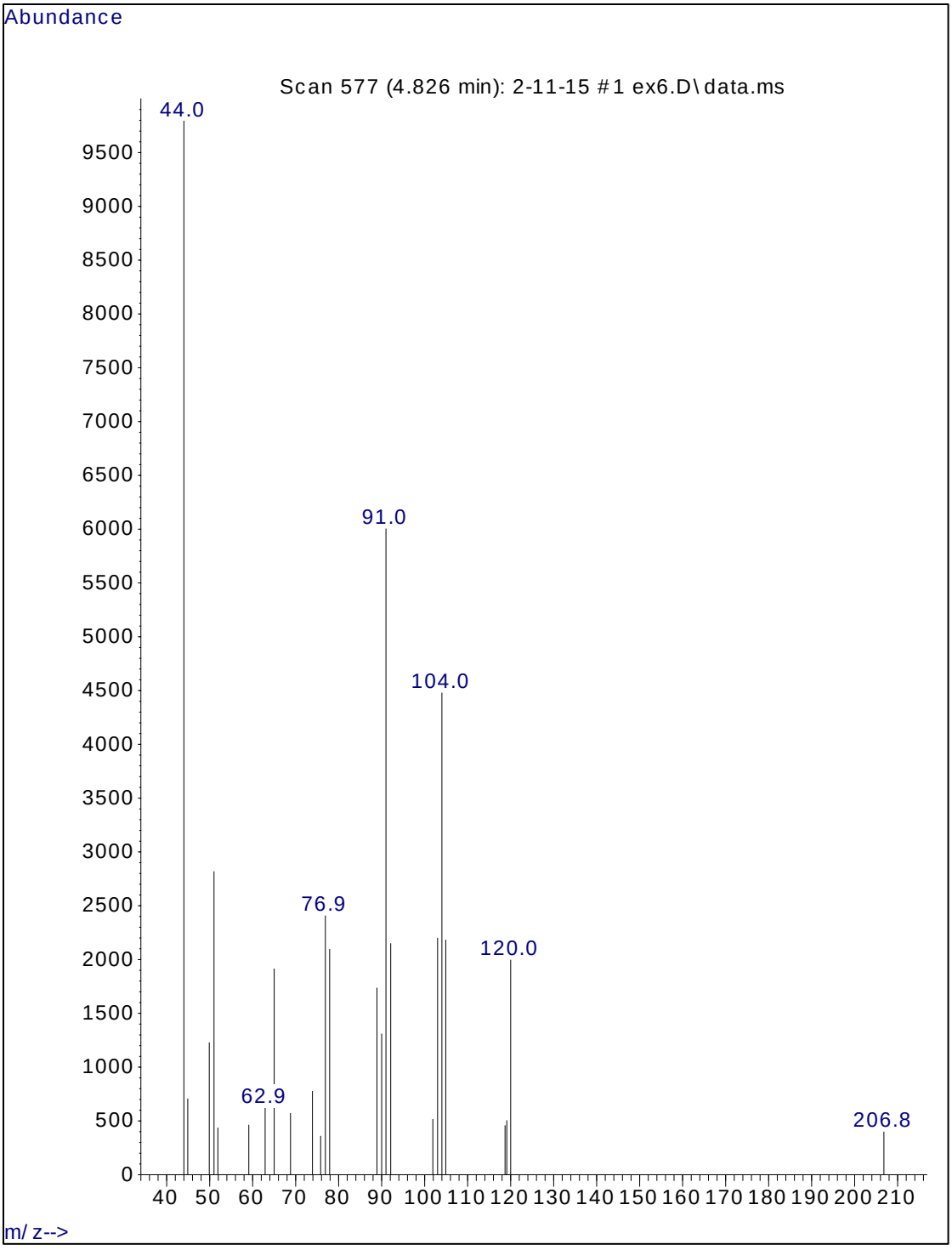


Figure 46. Mass spectrum for peak 3, Scheme 2. The reference spectrum is shown in Figure 47.

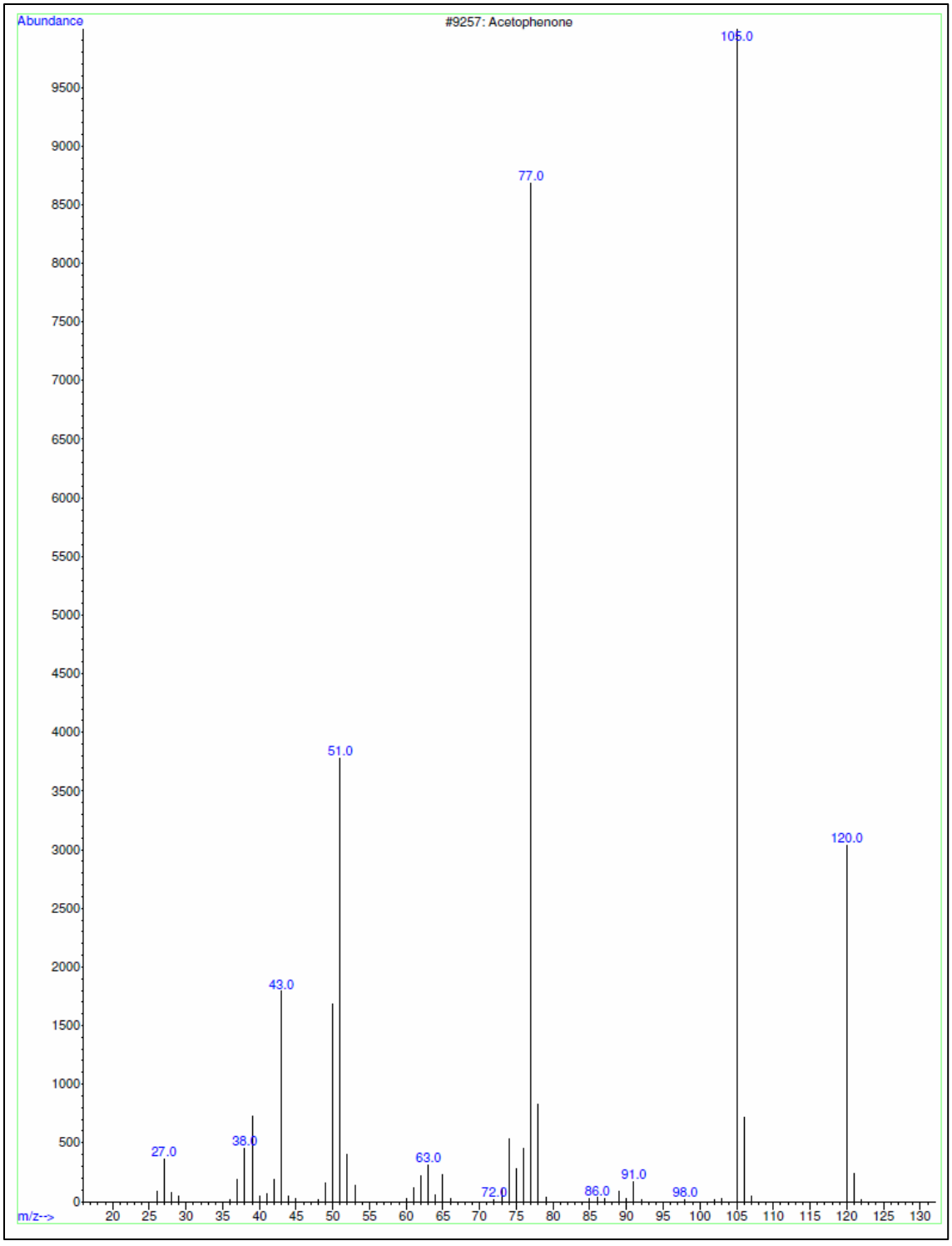


Figure 47. The identity of peak 3, Scheme 2, is acetophenone. This compound is also known as methyl phenyl ketone.

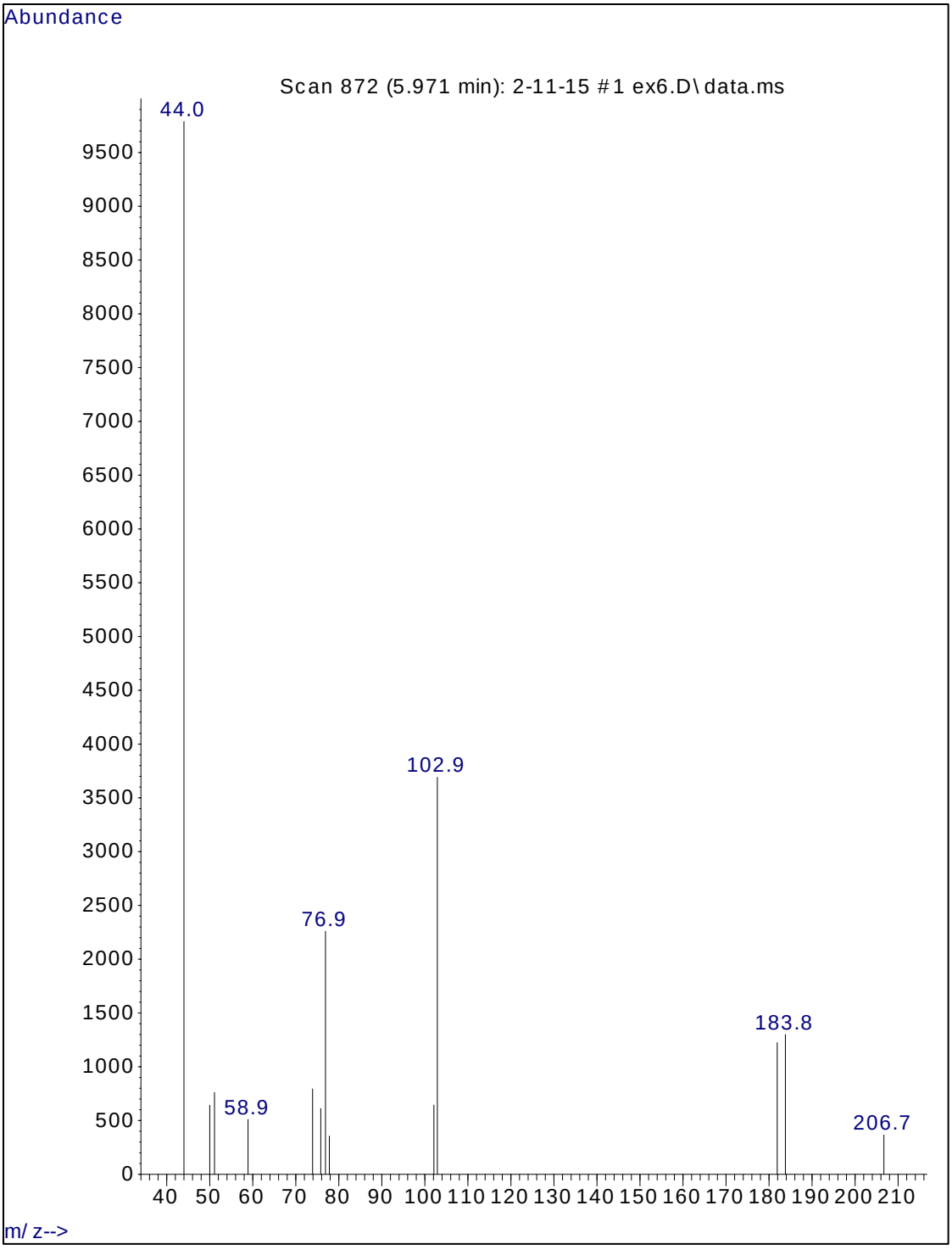


Figure 48. Mass spectrum for peak 4, Scheme 2. The reference spectrum is shown in Figure 49.

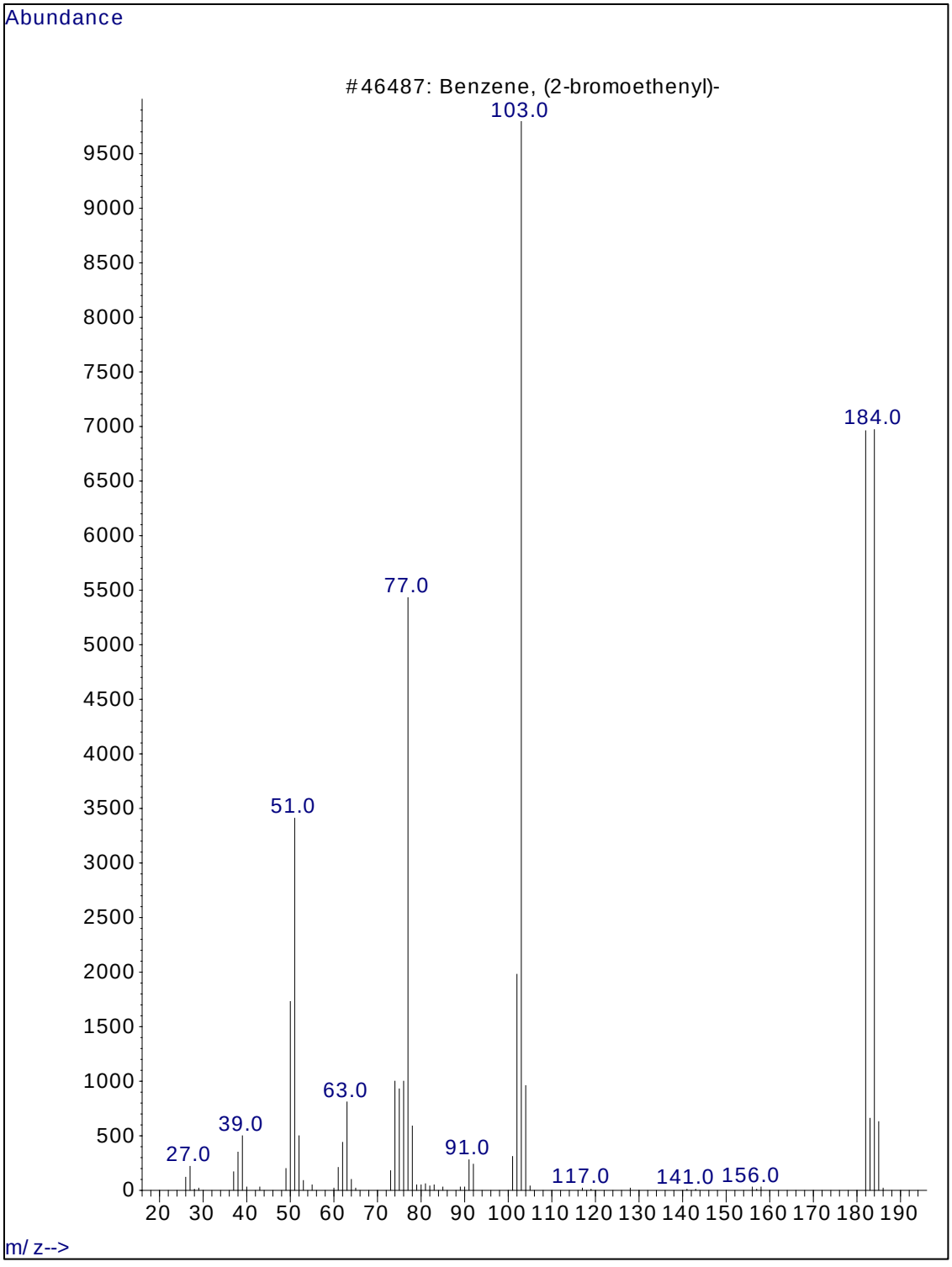


Figure 49. The identity of peak 4, Scheme 2, is (2-bromoethenyl)benzene.

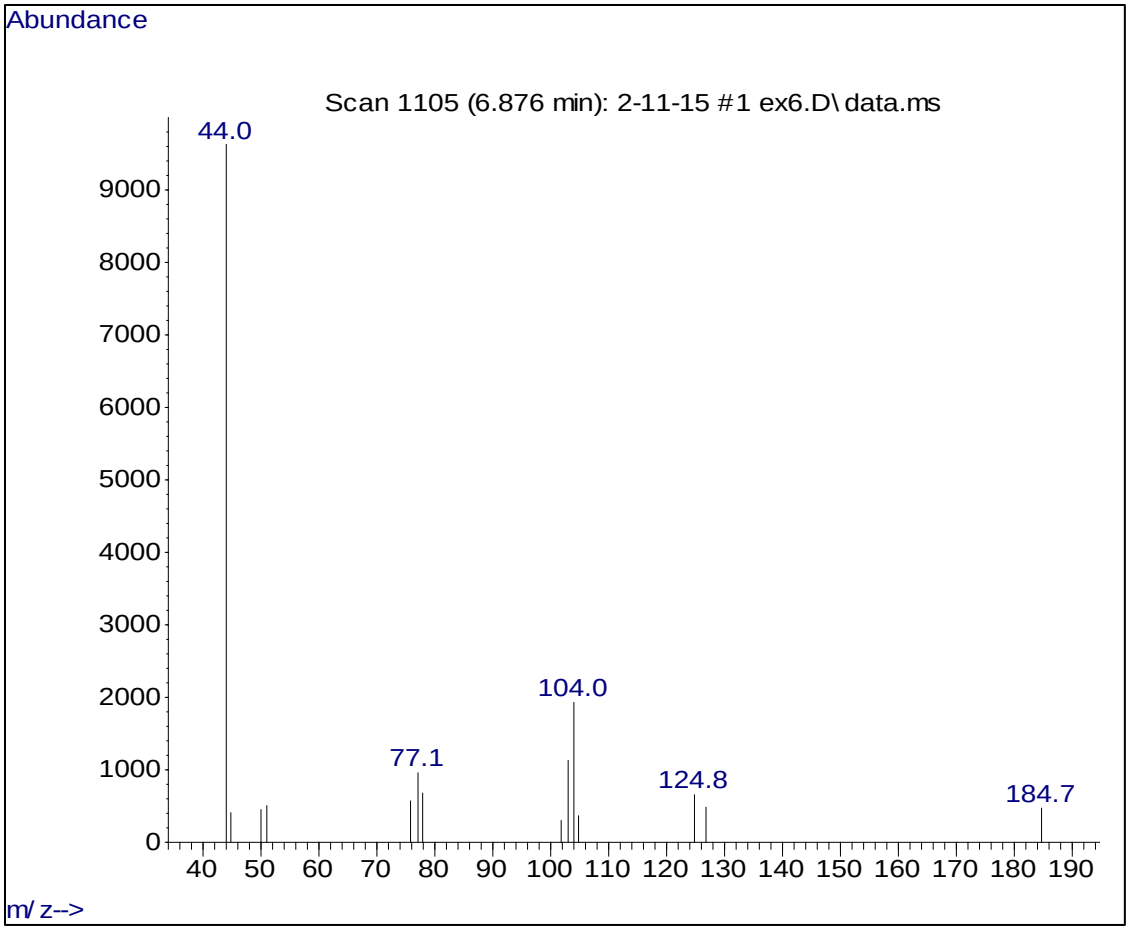


Figure 50. Mass spectrum of peak 5, Scheme 2. The compound is believed to be ß-bromo-benzeneethanol. No mass spectrum reference was found for this compound after an extensive literature search.

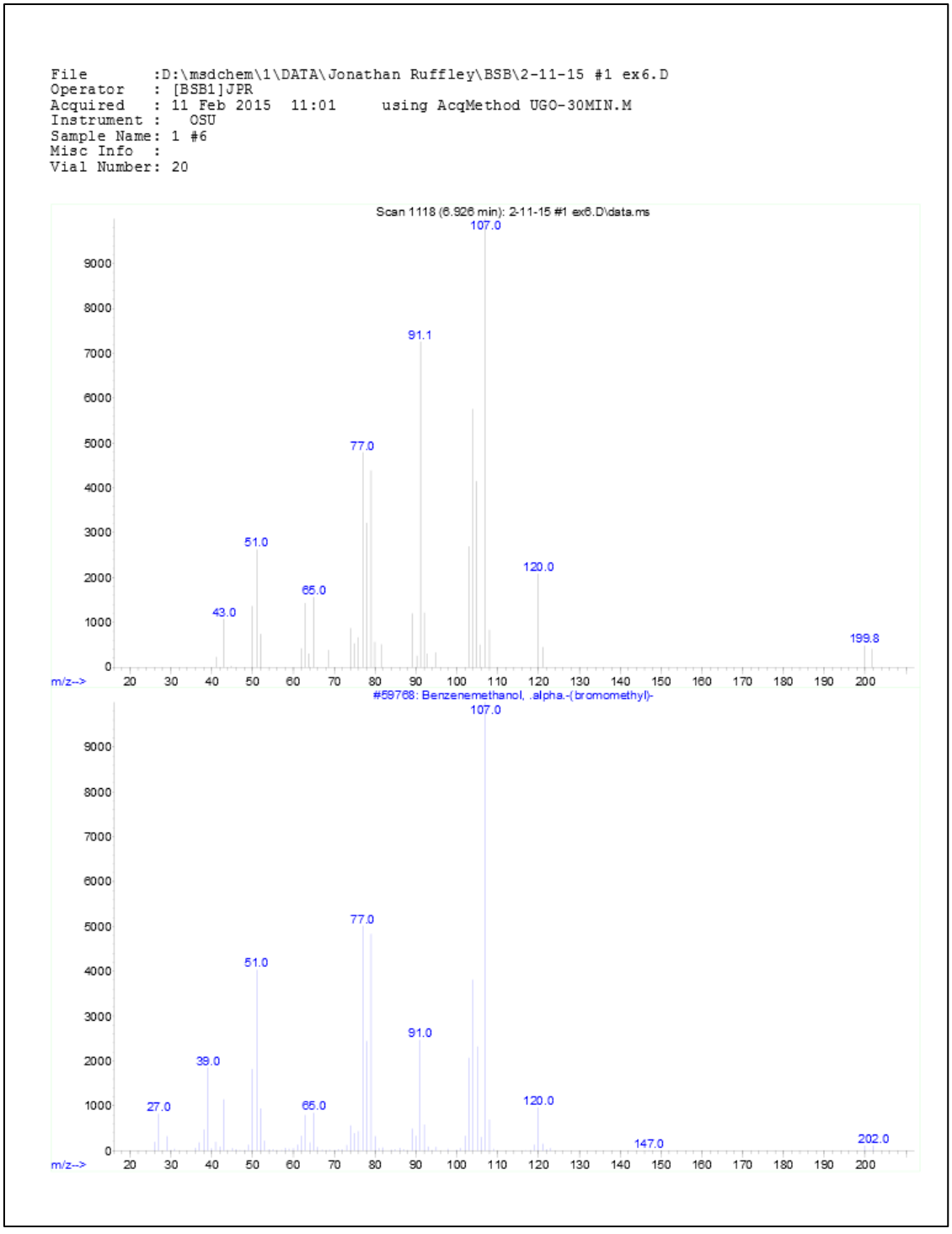


Figure 51. The identity of peak 6, Scheme 2, is α-(bromomethyl)-benzenemethanol.

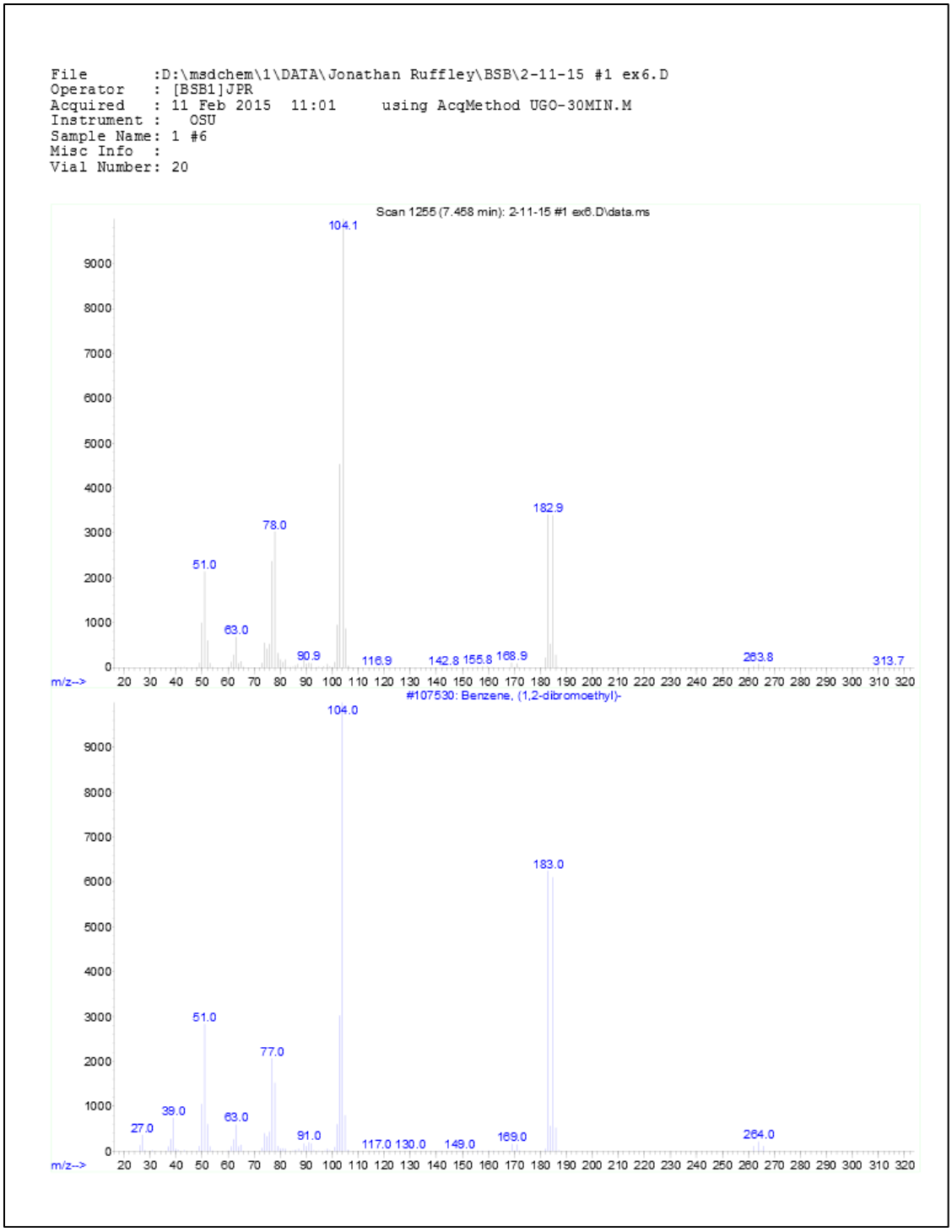


Figure 52. The identity of peak 7, Scheme 2, is (1,2-dibromoethyl)benzene.

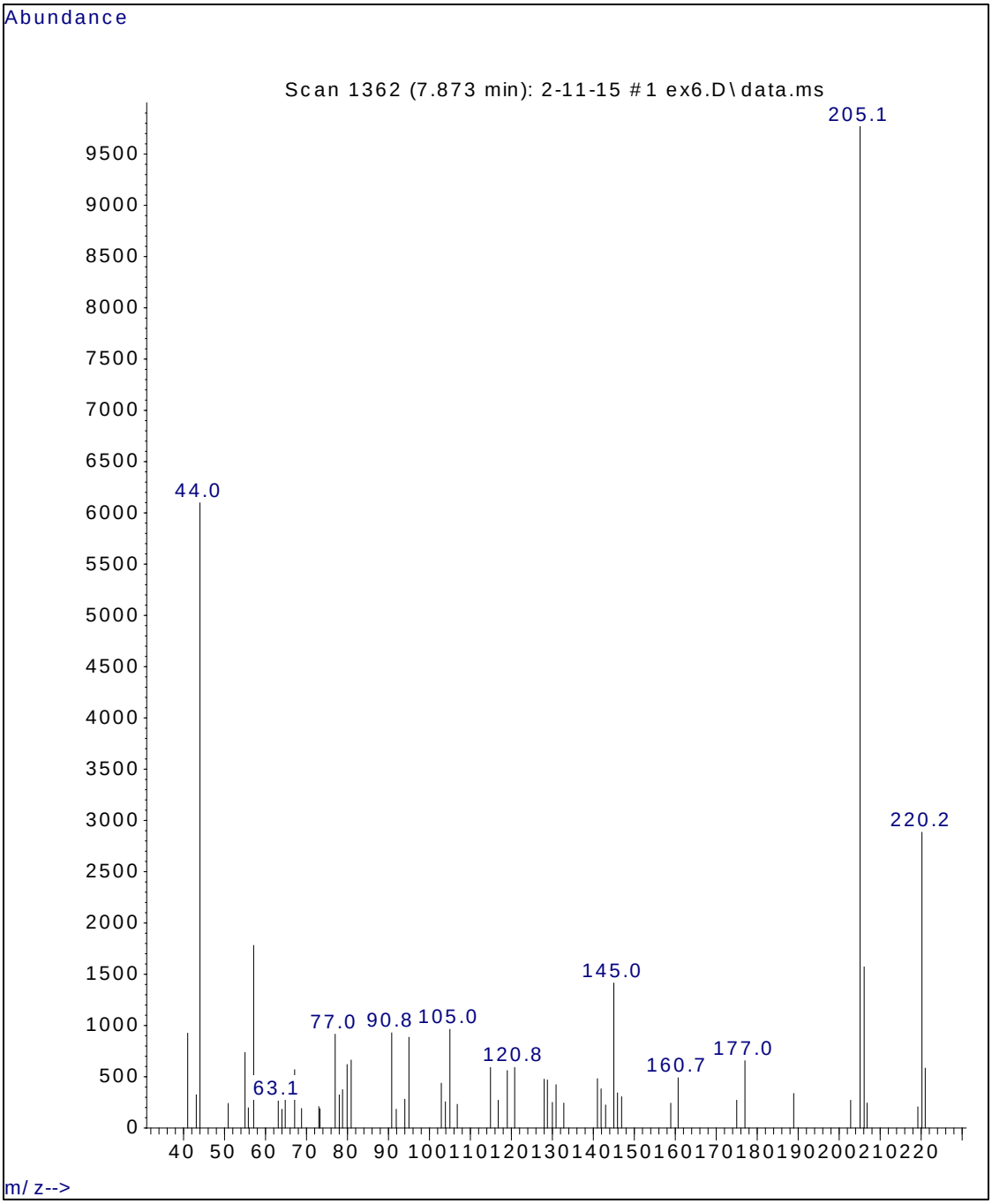


Figure 53. Mass spectrum of peak 8, Scheme 2. The reference spectrum is shown in Figure 54.

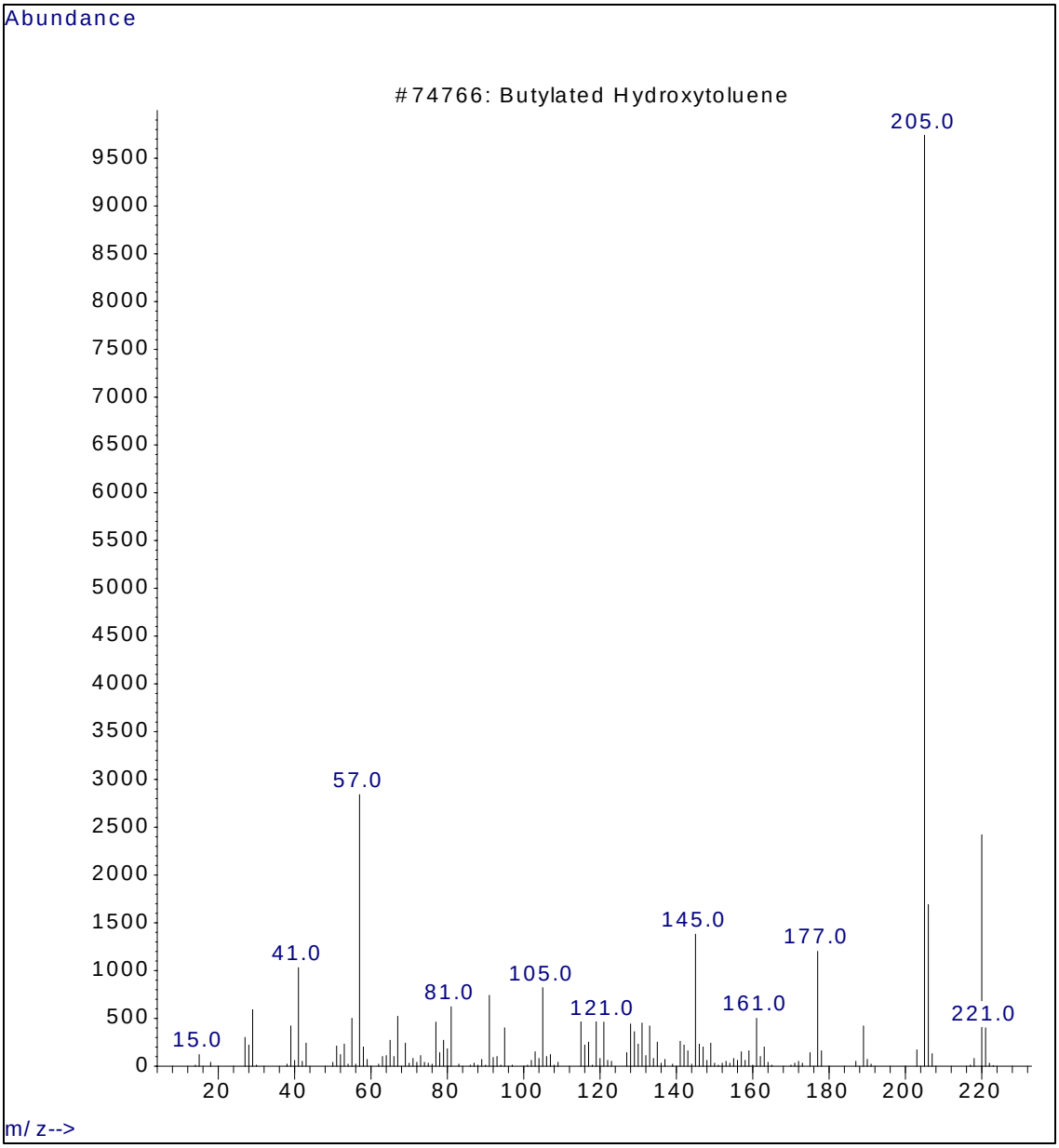


Figure 54. The identity of peak 8, Scheme 2, is butylated hydroxytoluene, or BHT. The presence of BHT in the sample likely results from its use as an inhibitor in the solvent used, diethyl ether (*20*).

Report 3. Area Percent Report for Scheme 3.

Area Percent Report

Data Path : D:\msdchem\1\DATA\Jonathan Ruffley\
Data File : 2-11-15 #1 ex7.D
Acq On : 11 Feb 2015 11:37
Operator : JPR
Sample : 1 #7
Misc :
ALS Vial : 21 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : D:\msdchem\1\METHODS\UGO-30min.M
Title :

Signal : TIC: 2-11-15 #1 ex7.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.040	108	117	169	PH	1153696	35527046	66.13%	83.994%
2	3.642	258	272	289	BV	55060	620026	1.15%	1.466%
3	5.483	737	746	752	VV 2	16192	193793	0.36%	0.458%
4	5.970	846	872	882	BV 6	7365	130037	0.24%	0.307%
5	7.457	1242	1255	1298	PV 2	4962989	53719911	100.00%	127.005%
6	10.825	2099	2123	2132	PV 2	8140	160832	0.30%	0.380%
7	11.921	2383	2405	2478	PV	618090	13834906	25.75%	32.709%
8	16.083	3419	3477	3482	BBA	2073214	-61889209	-115.21%	-146.319%

Sum of corrected areas: 42297342

UGO-30min.M Wed Mar 04 22:13:49 2015

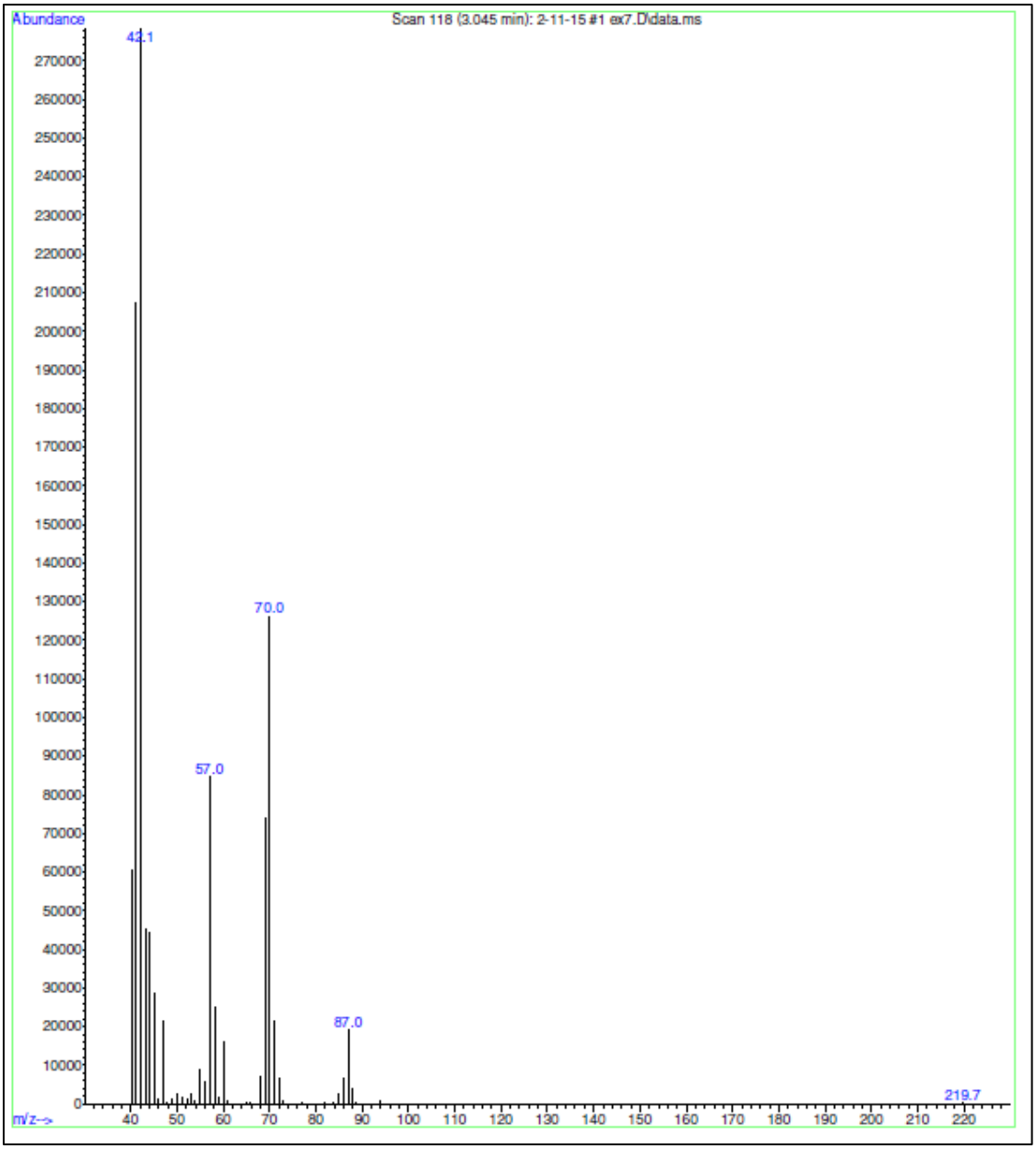


Figure 55. The identity of this product is unknown.

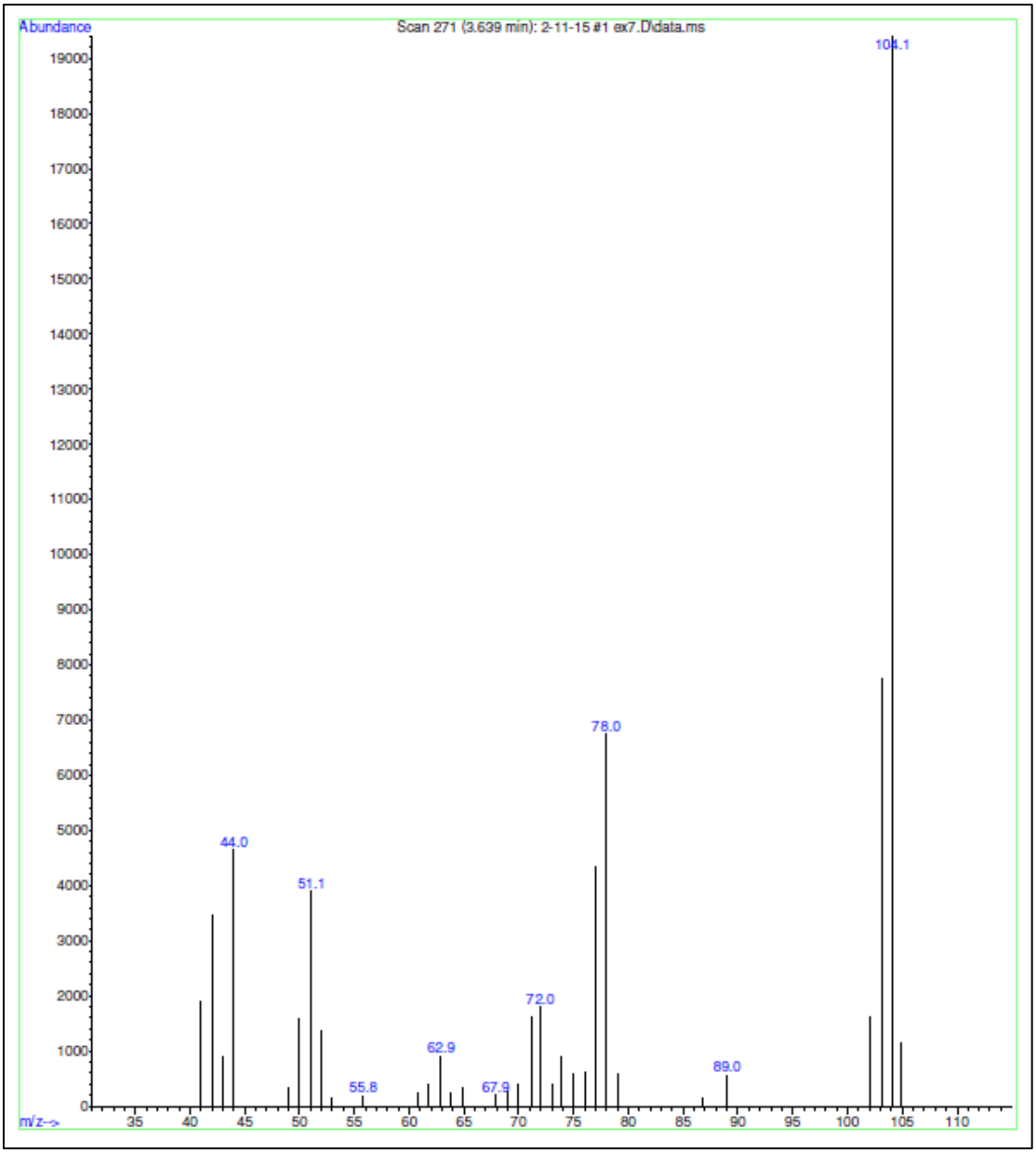


Figure 56. The identity of peak 2 is styrene. The reference spectrum can be seen in Figure 57.

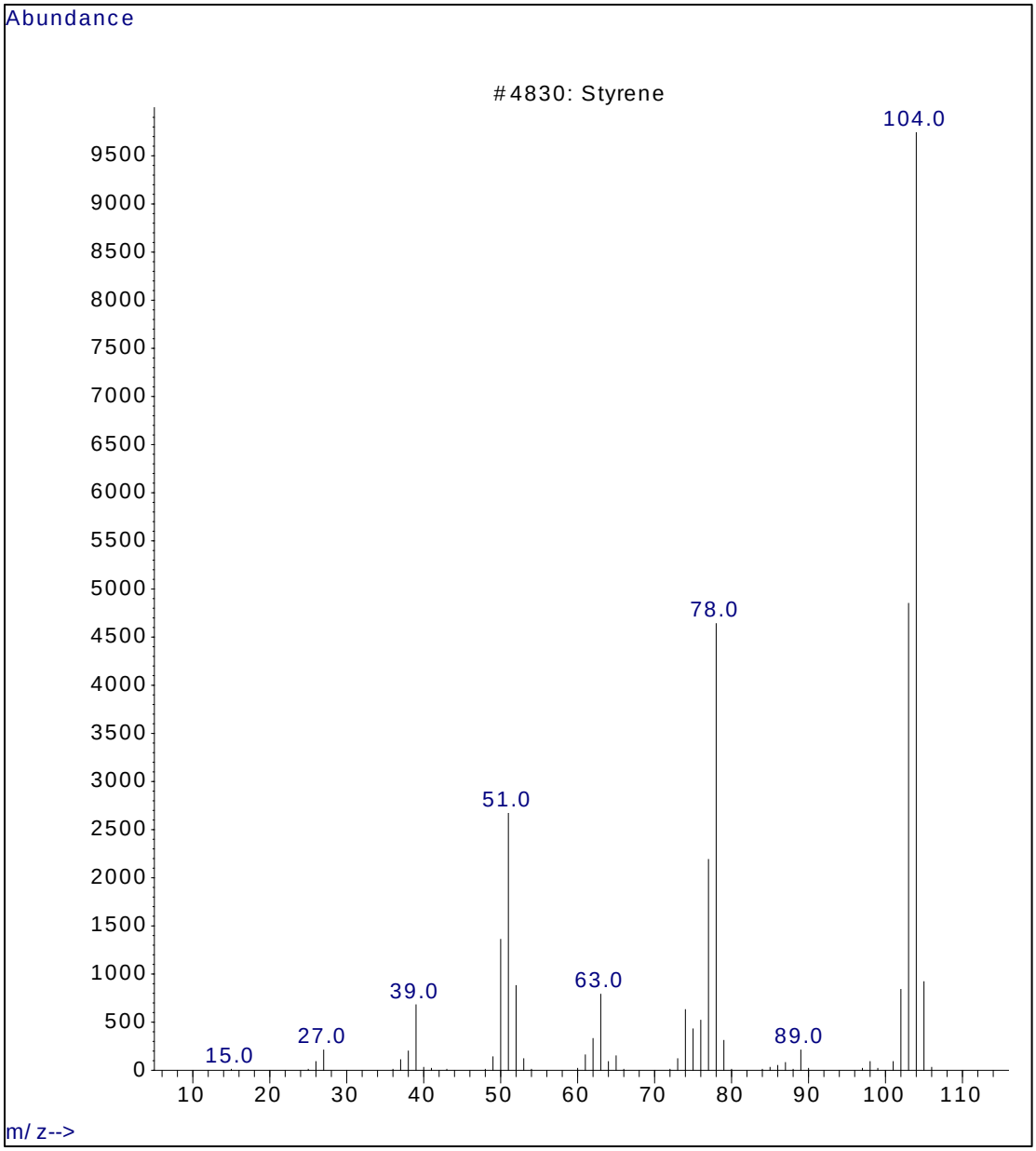


Figure 57. Reference spectrum for peak 2.

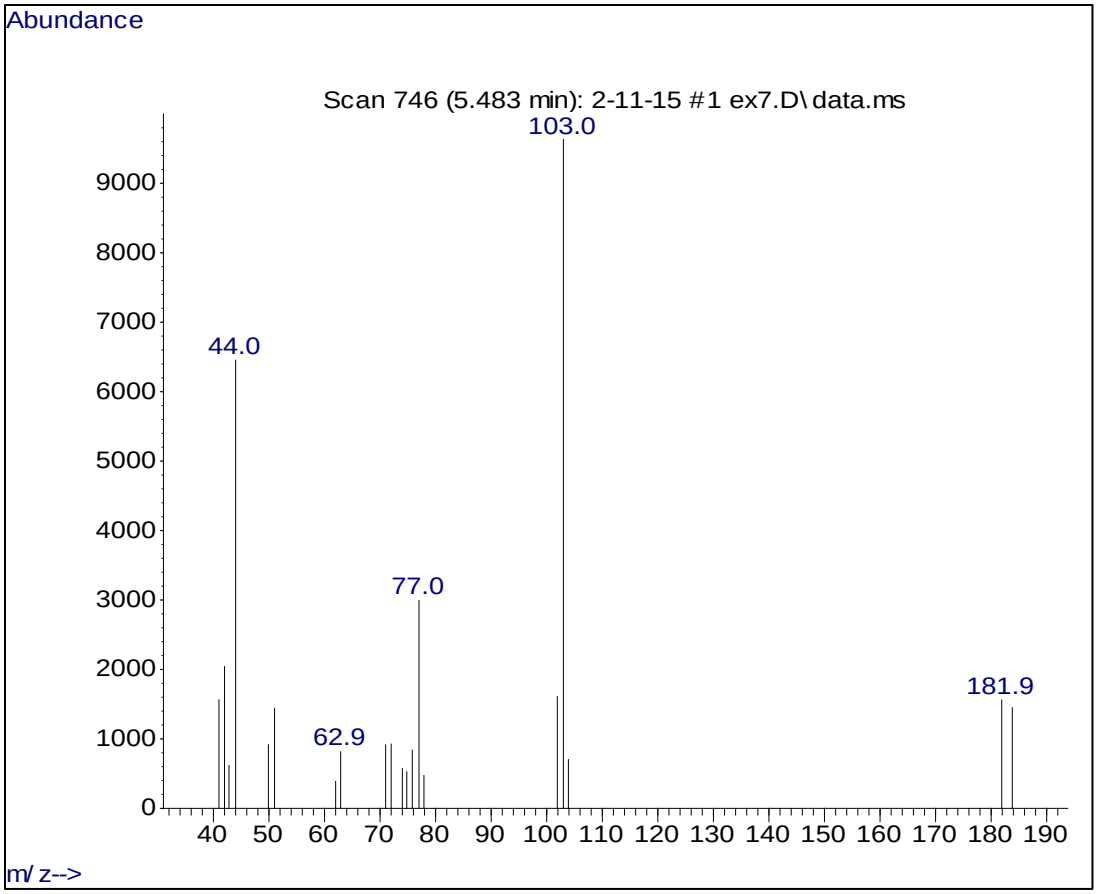


Figure 58. The identity of peak 3 is (1-bromoethenyl)benzene. See Figure 59 for the reference spectrum.

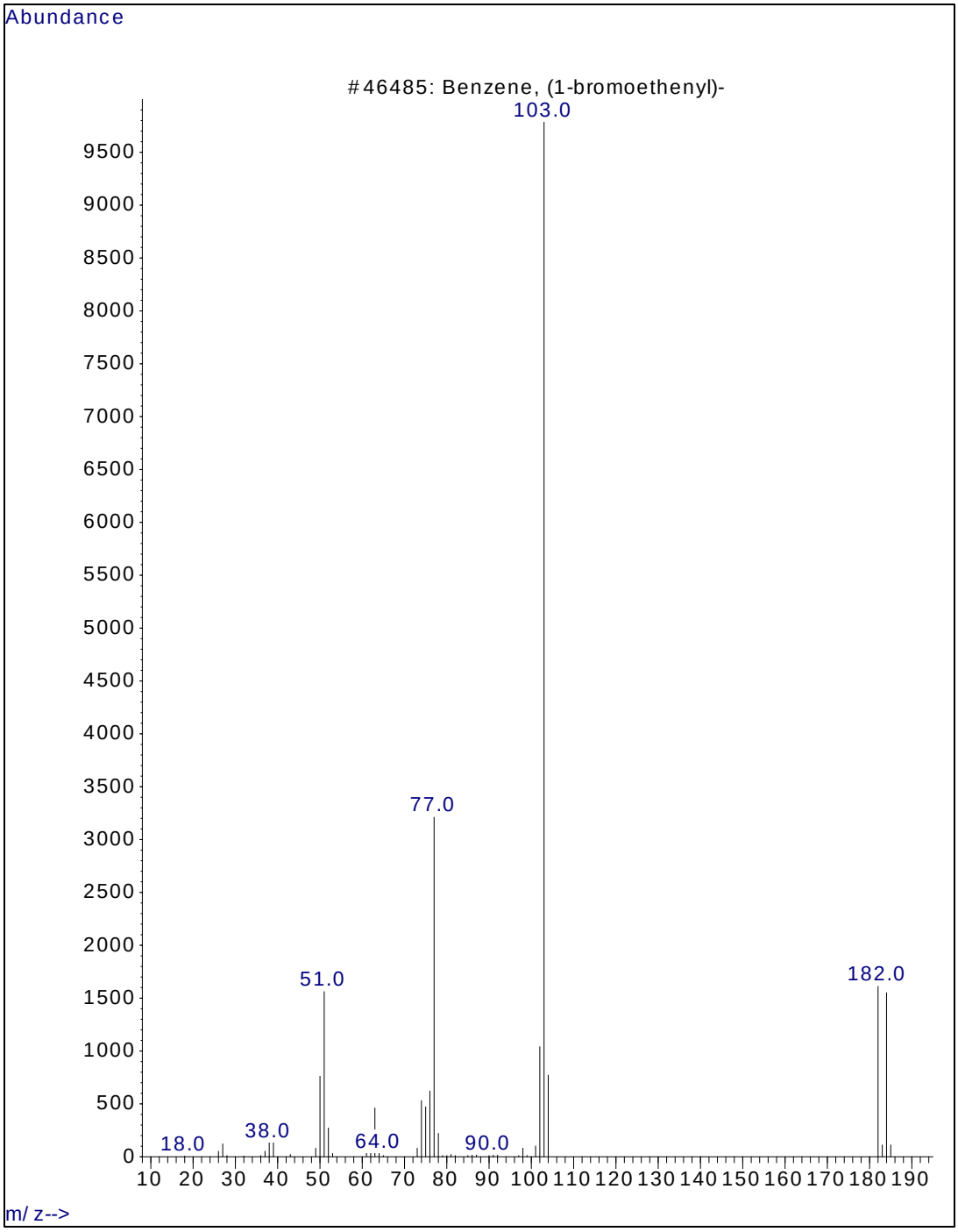


Figure 59. Reference spectrum for peak 3.

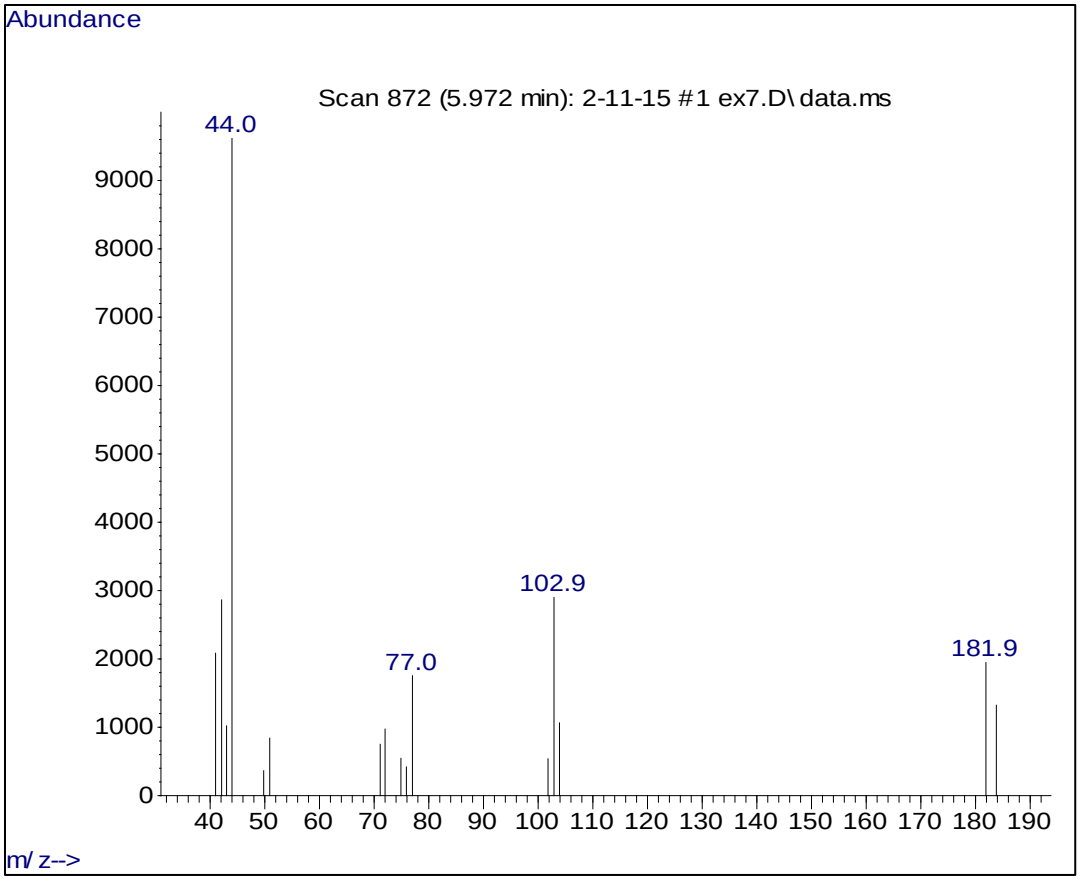


Figure 60. The identity of peak 4 is (2-bromoethenyl)benzene. See Figure 61 for the reference spectrum.

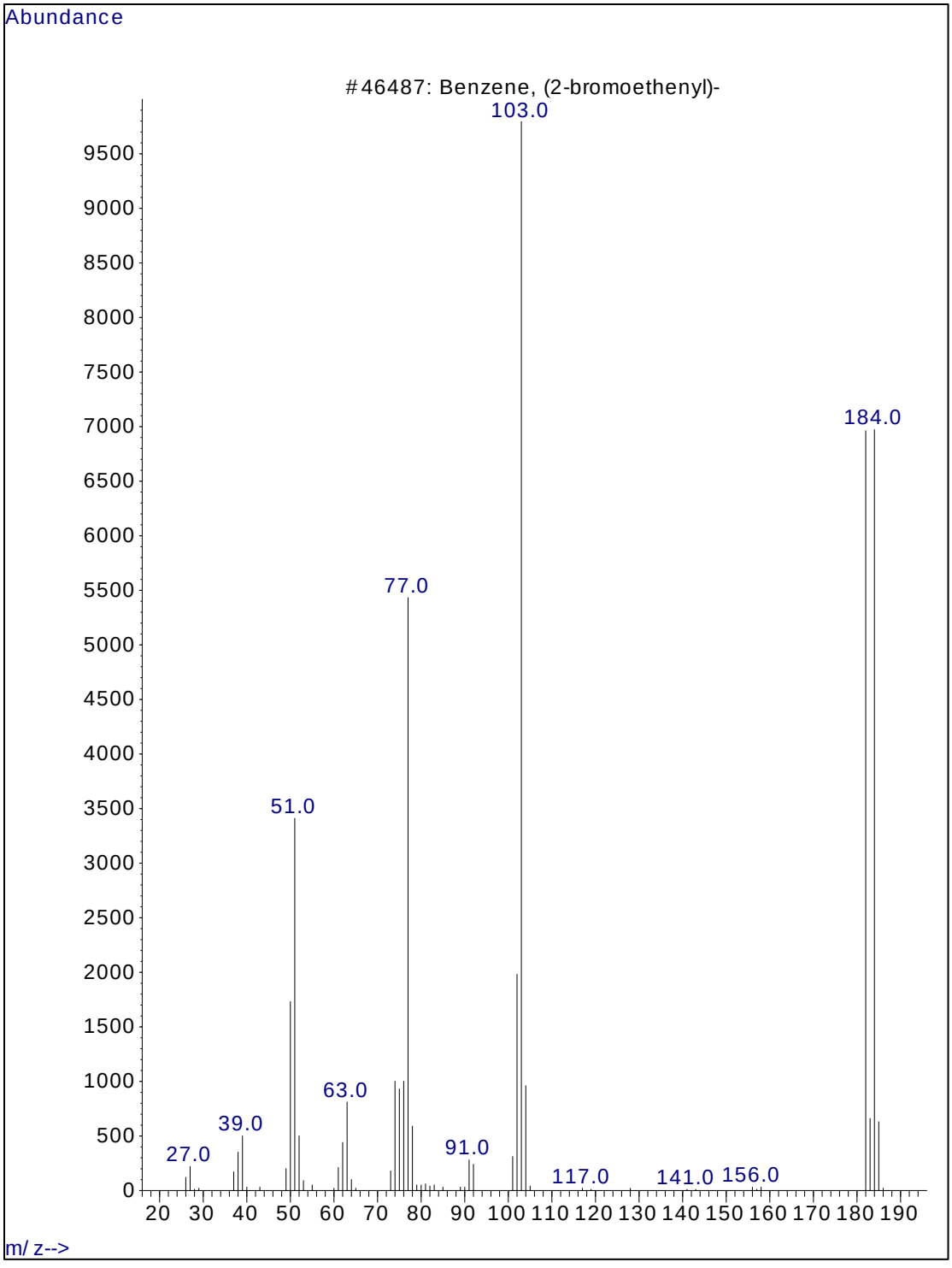


Figure 61. Reference spectrum for peak 4.

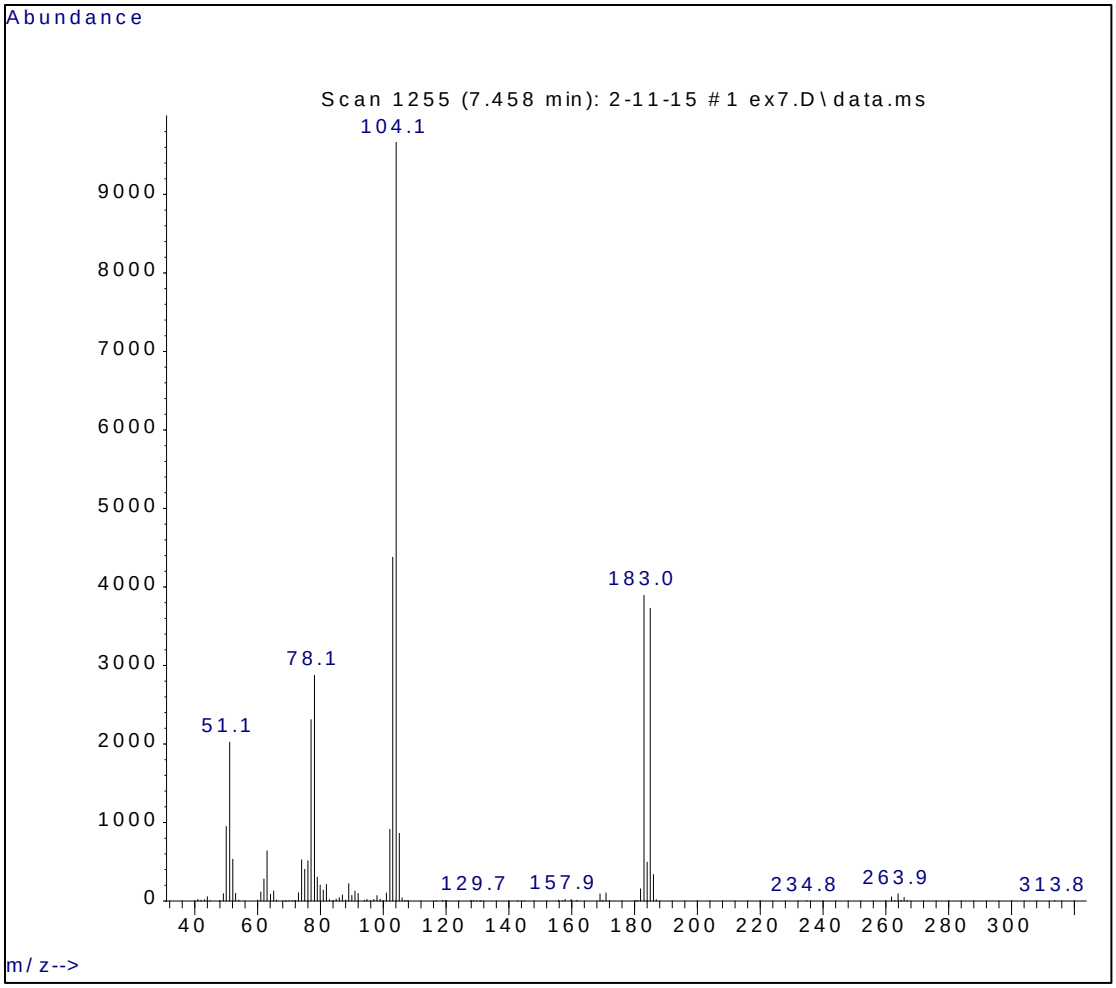


Figure 62. The identity of peak 5 is (1,2-dibromoethyl)benzene. See Figure 63 for the reference spectrum.

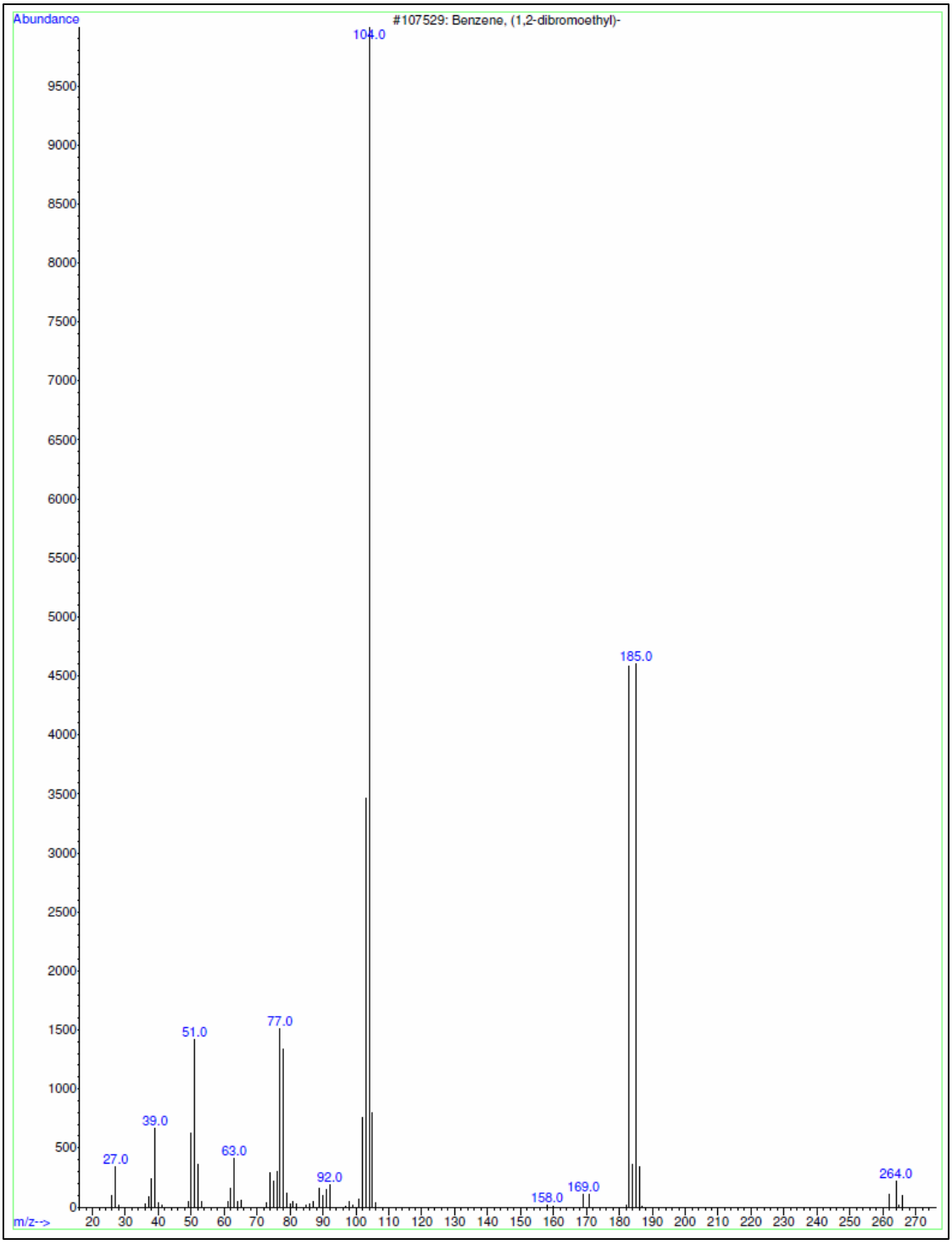


Figure 63. Reference spectrum for peak 5.

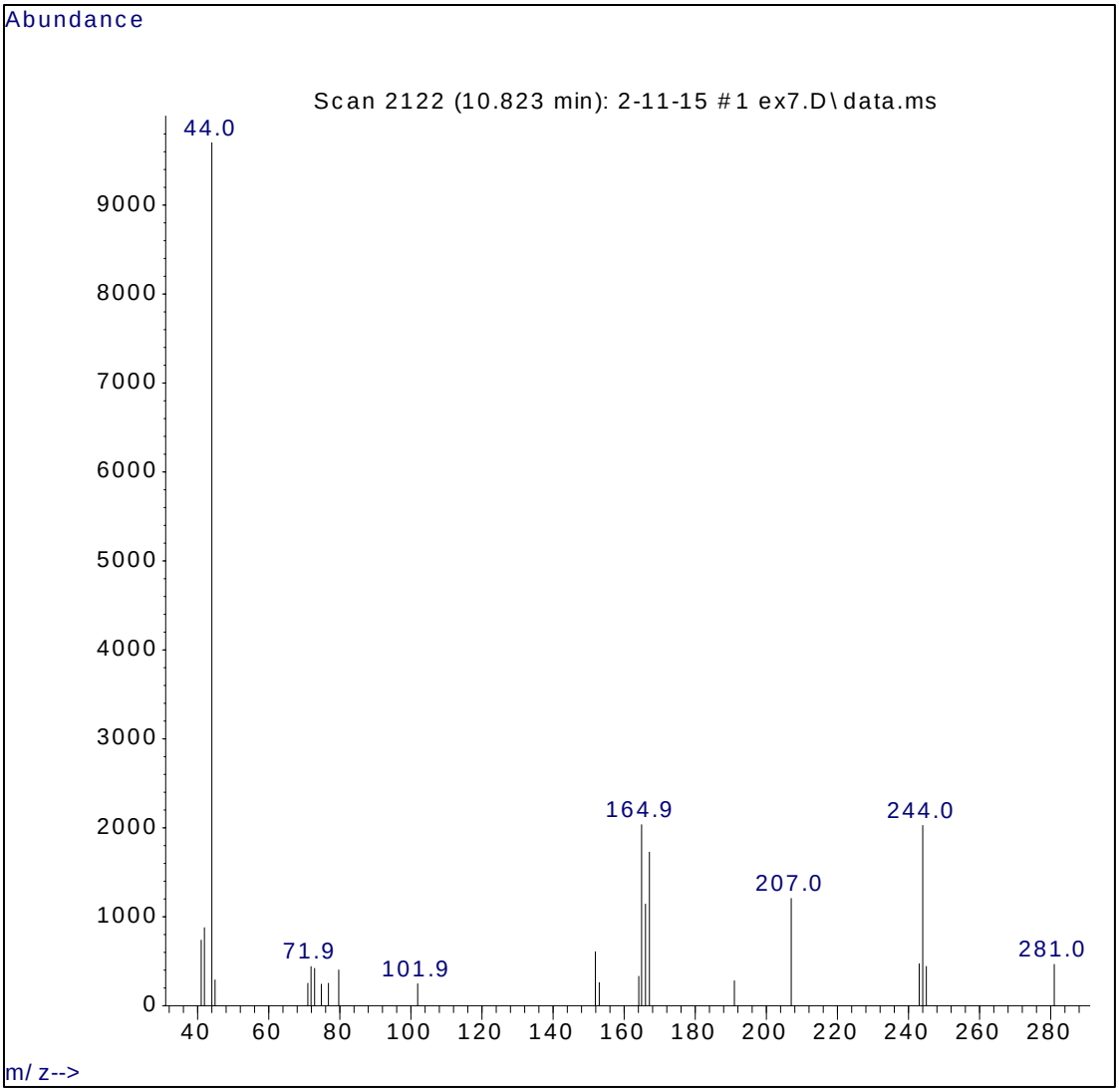


Figure 64. The identity of peak 6 is unknown.

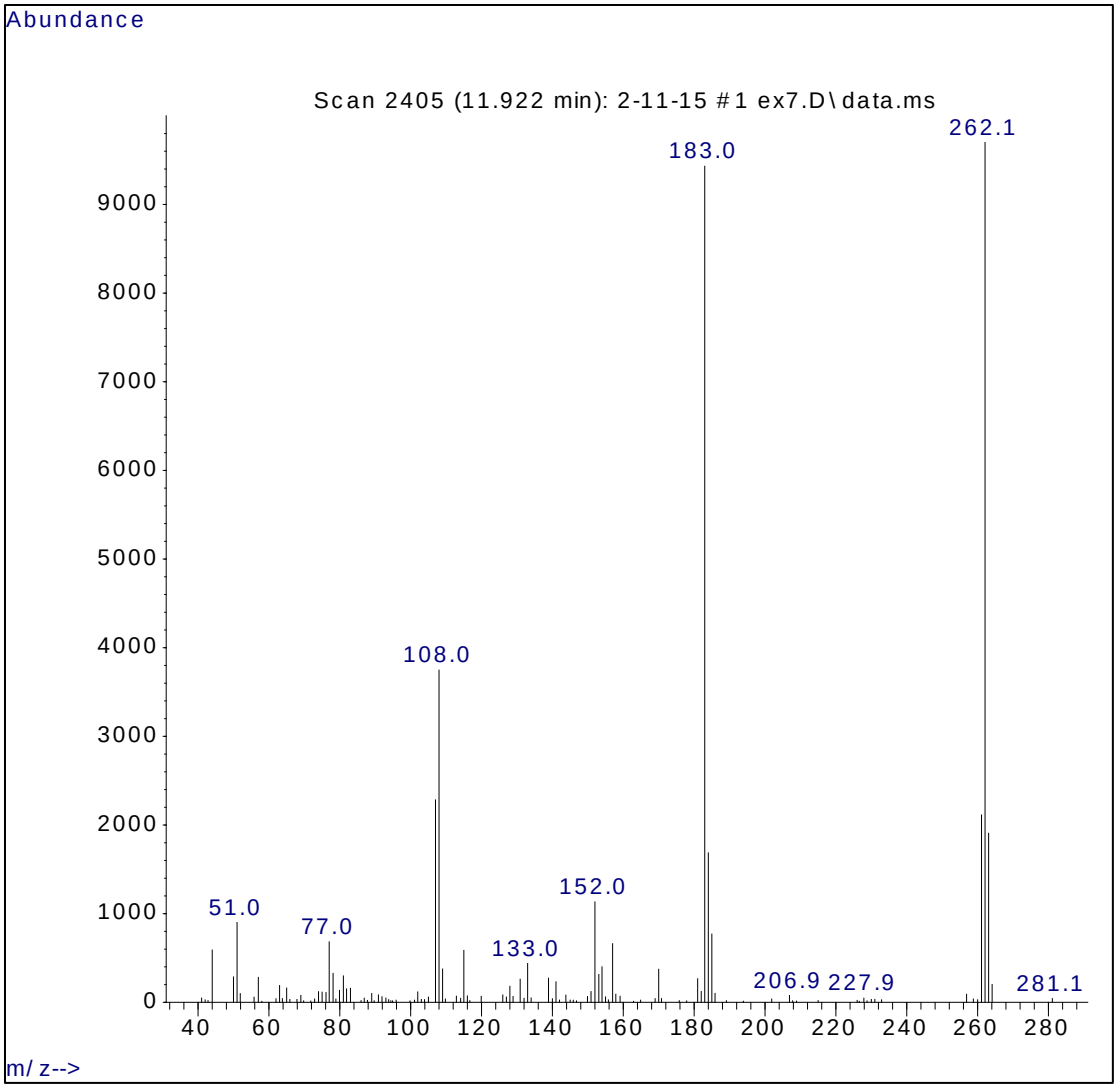


Figure 65. The identity of peak 7 is triphenylphosphine. See Figure 66 for the reference spectrum.

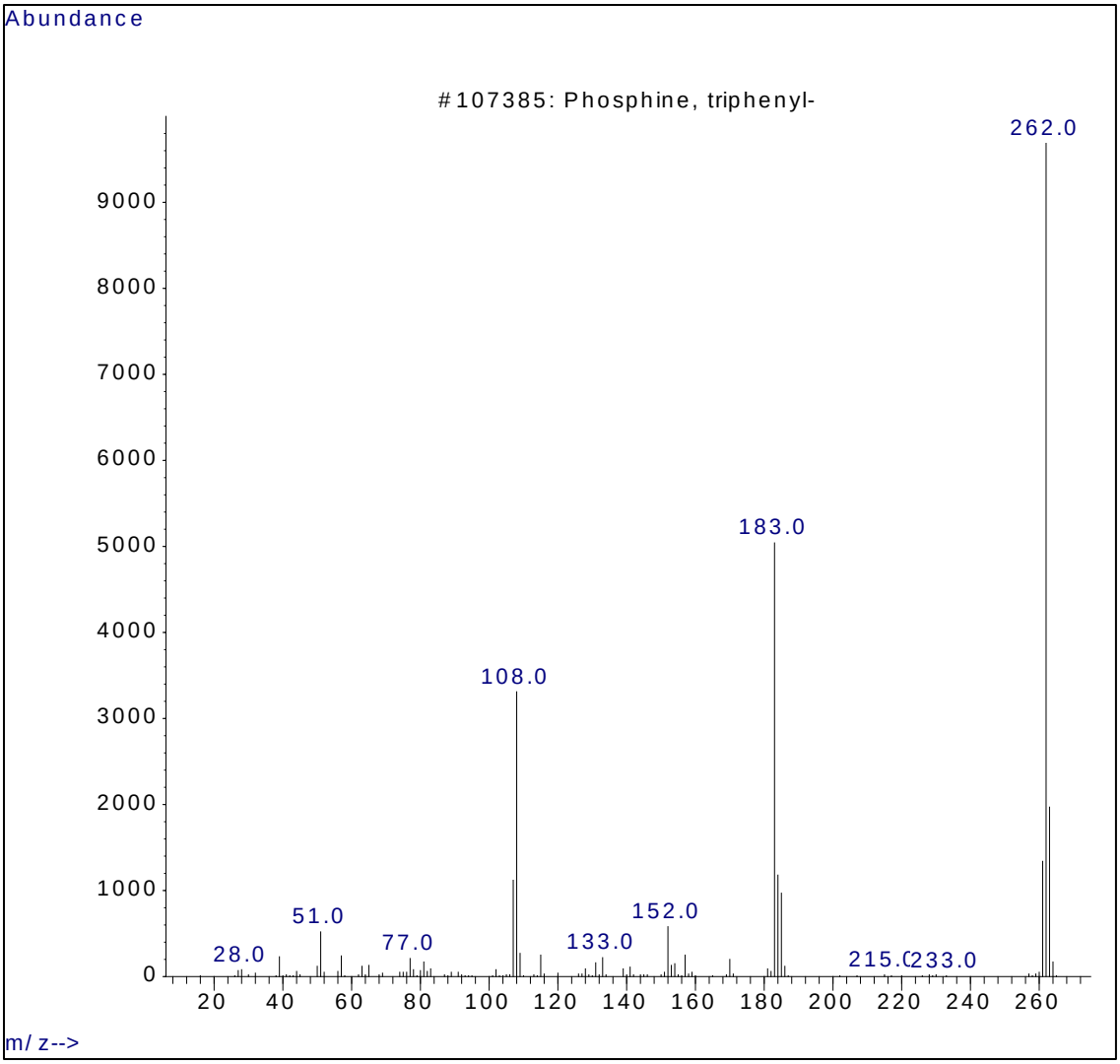


Figure 66. Reference spectrum for peak 7.

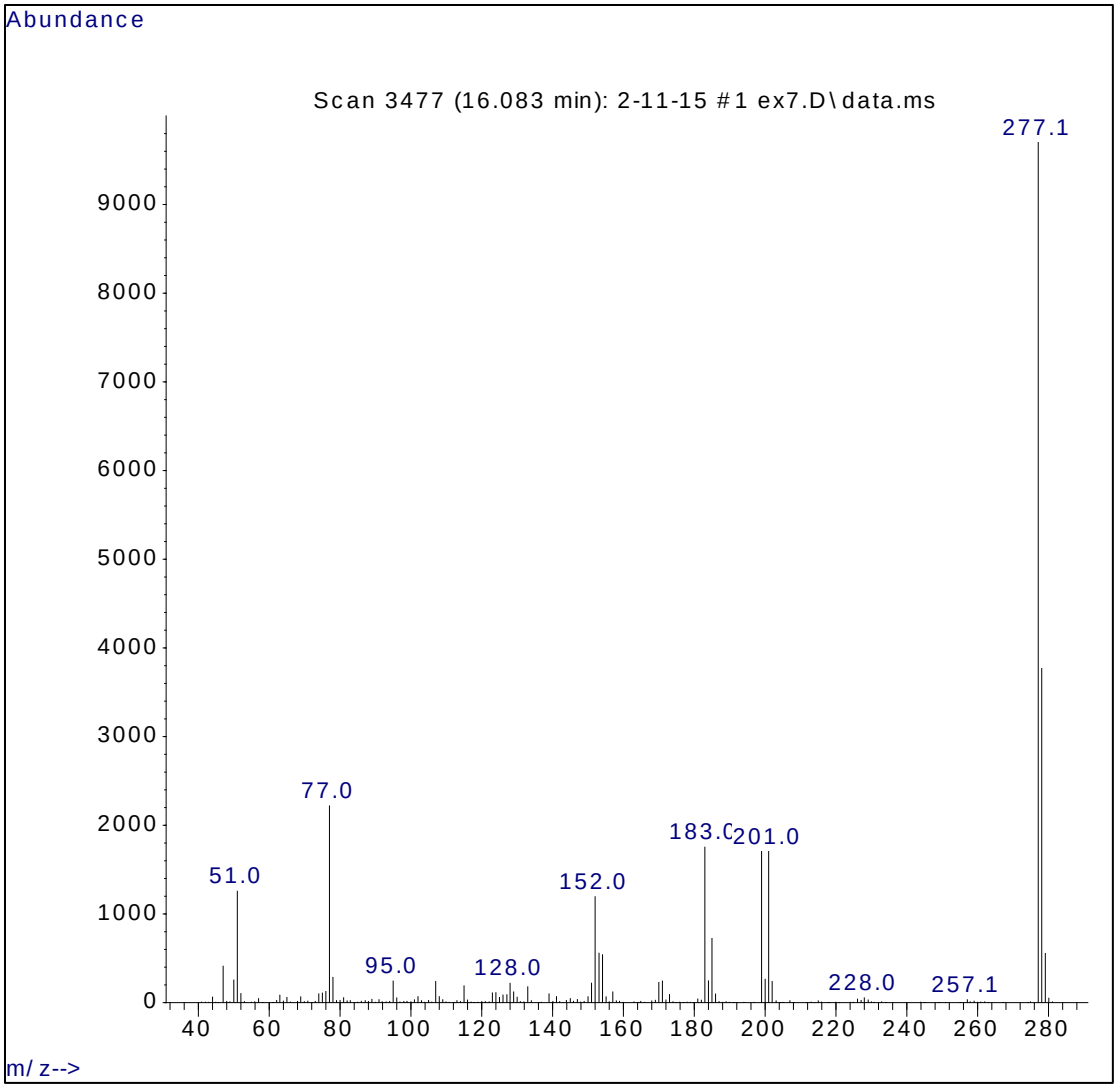


Figure 67. Peak 8 was expected to contain the phosphonium salt products. The peak did not resolve well on the instrument.

Report 4. Area percent report for Scheme 4.

```
Area Percent Report

  Data Path : D:\msdchem\1\DATA\Jonathan Ruffley\
  Data File : 2-11-15 #1 ex8.D
  Acq On    : 11 Feb 2015  12:13
  Operator  : JPR
  Sample    : 1 #8
  Misc      :
  ALS Vial  : 22   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\msdchem\1\METHODS\UGO-30min.M
  Title     :

  Signal     : TIC: 2-11-15 #1 ex8.D\data.ms
```

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	3.048	108	119	179	PH 3	123658	5271176	57.42%	20.365%
2	3.644	264	272	281	PV 4	7443	100515	1.09%	0.388%
3	3.719	285	292	295	VV	150785	1726157	18.80%	6.669%
4	3.750	295	300	335	VV	456447	5472126	59.61%	21.141%
5	5.482	736	746	768	VV	869200	9180033	100.00%	35.467%
6	5.968	856	871	884	BV 2	38562	442433	4.82%	1.709%
7	7.457	1240	1255	1266	PBA2	322081	3691094	40.21%	14.260%

```
                        Sum of corrected areas:    25883534

UGO-30min.M Wed Mar 04 22:25:06 2015
```

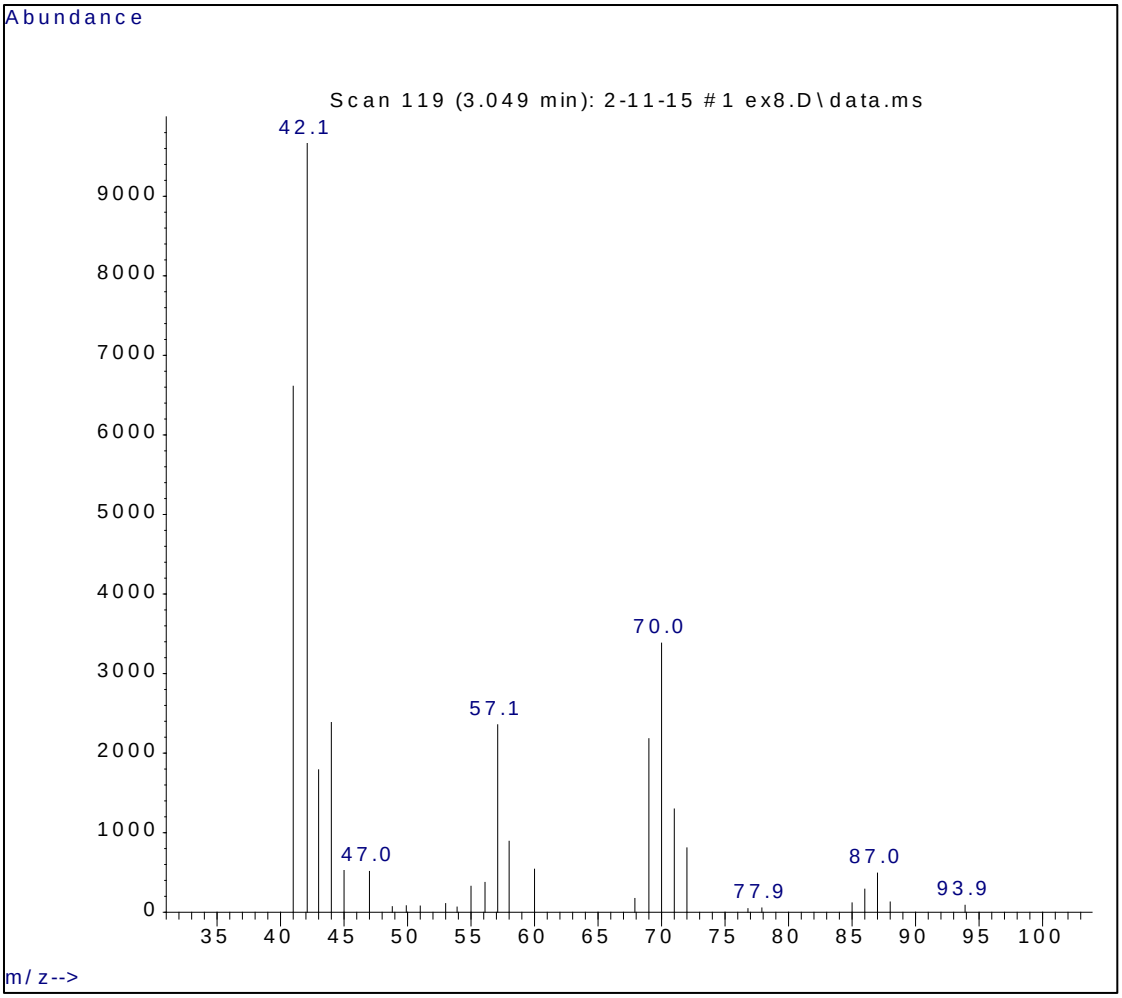


Figure 68. The identity of peak 1 was tetrahydro-2-furanol. See Figure 69 for the reference spectrum.

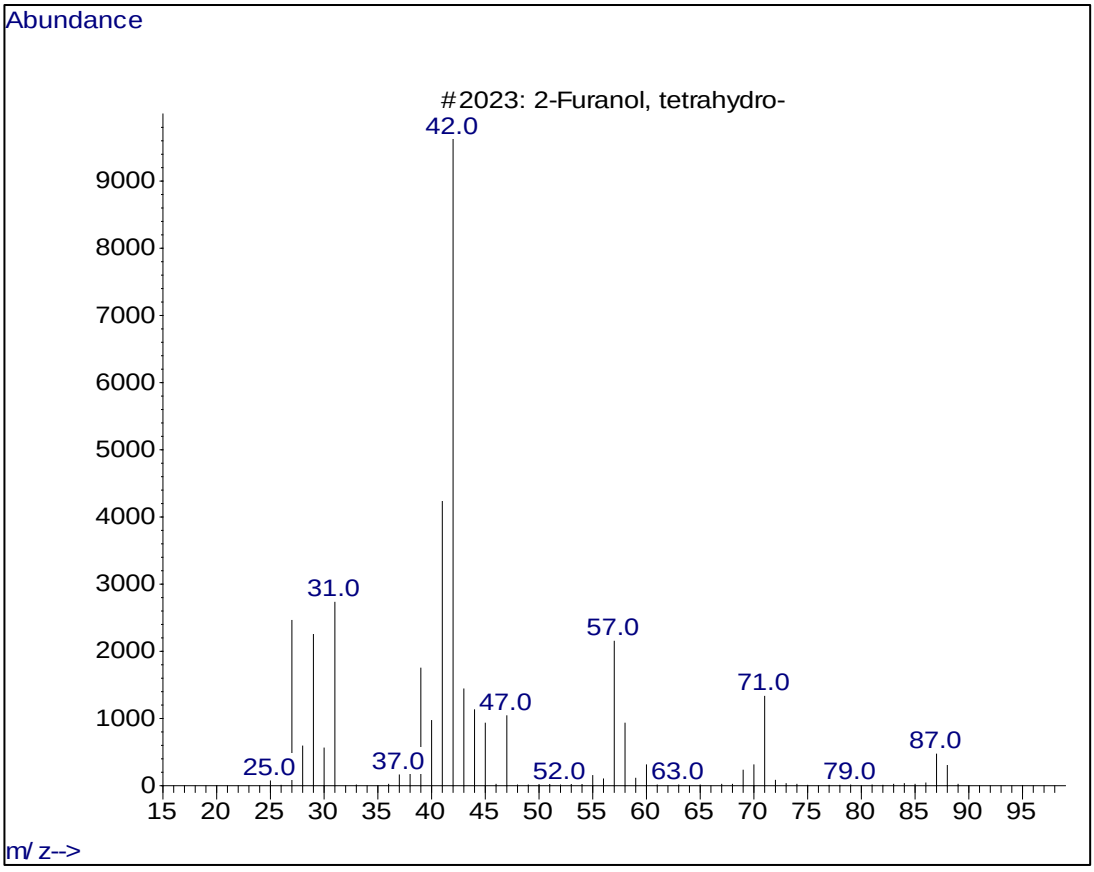


Figure 69. Reference spectrum for peak 1.

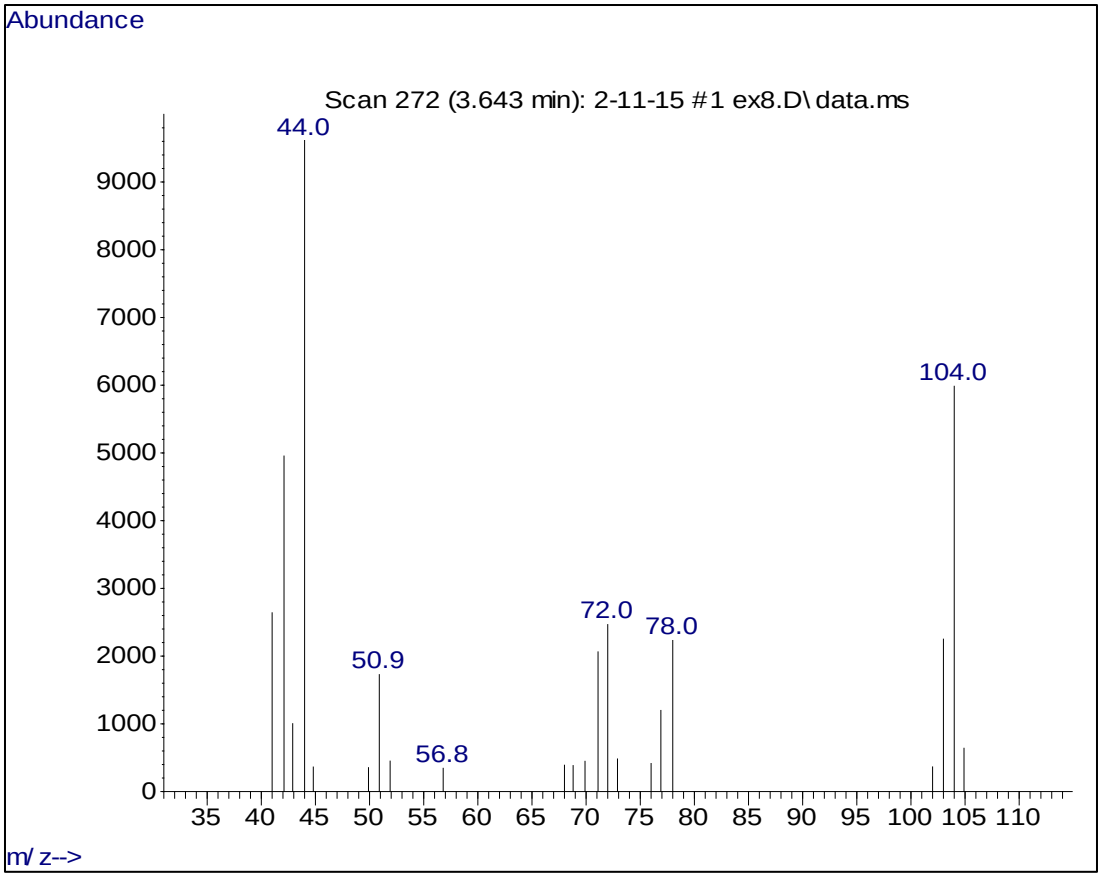


Figure 70. The identity of peak 2 was styrene. See Figure 71 for the reference spectrum.

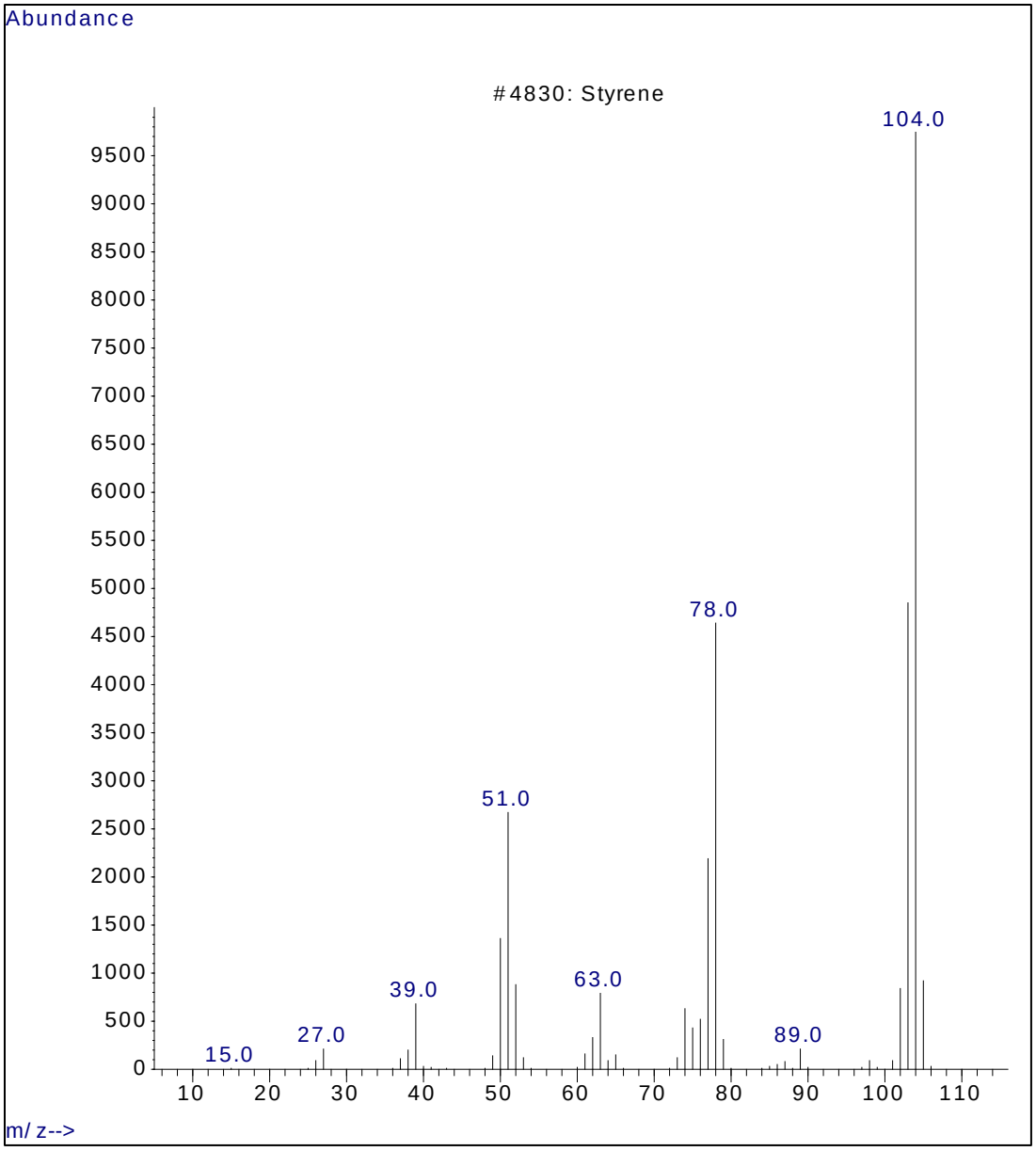


Figure 71. Reference spectrum for peak 2.

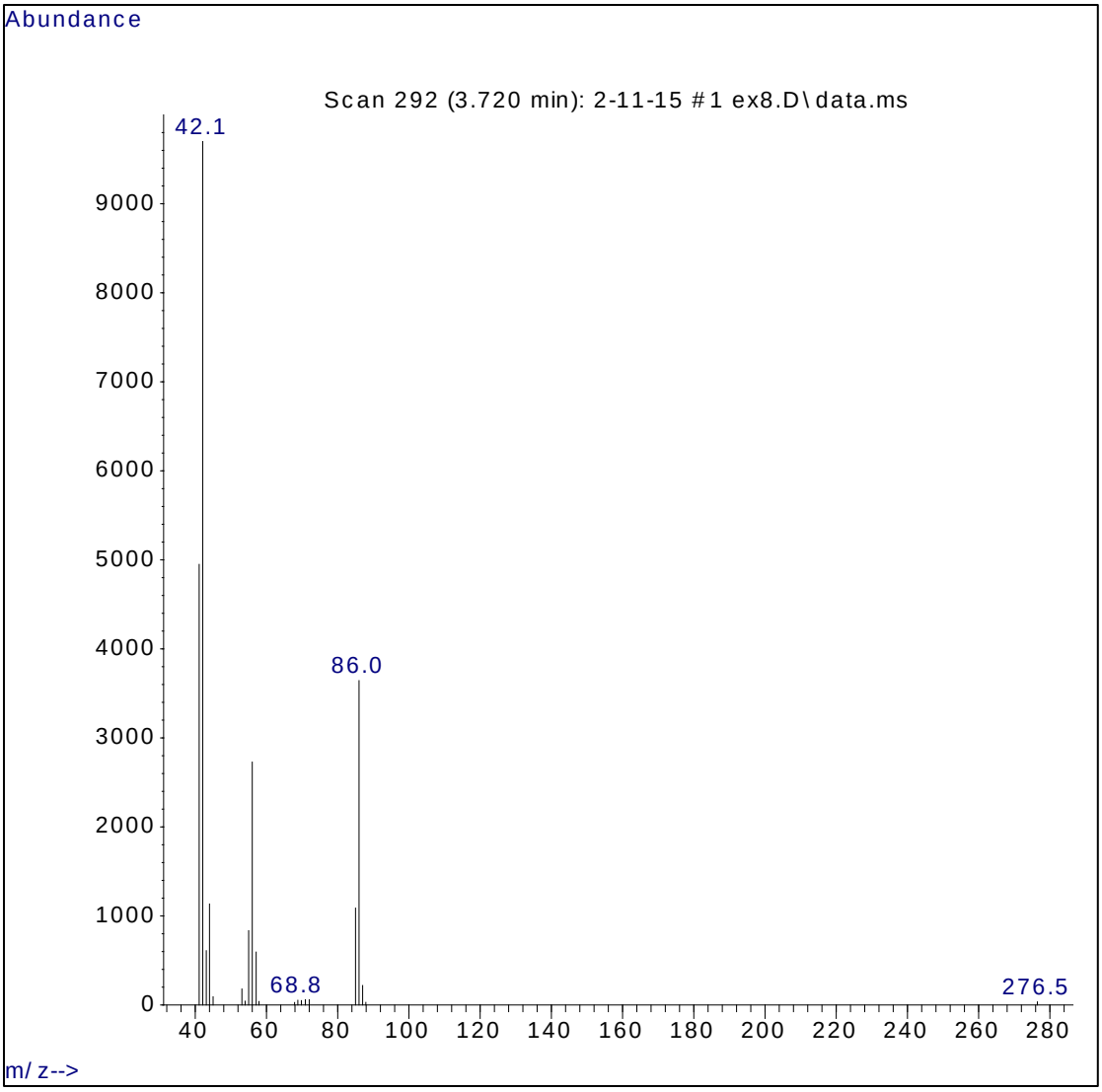


Figure 72. The identity of peak 3 was butyrolactone, which is a derivative of THF. See Figure 73 for the reference spectrum.

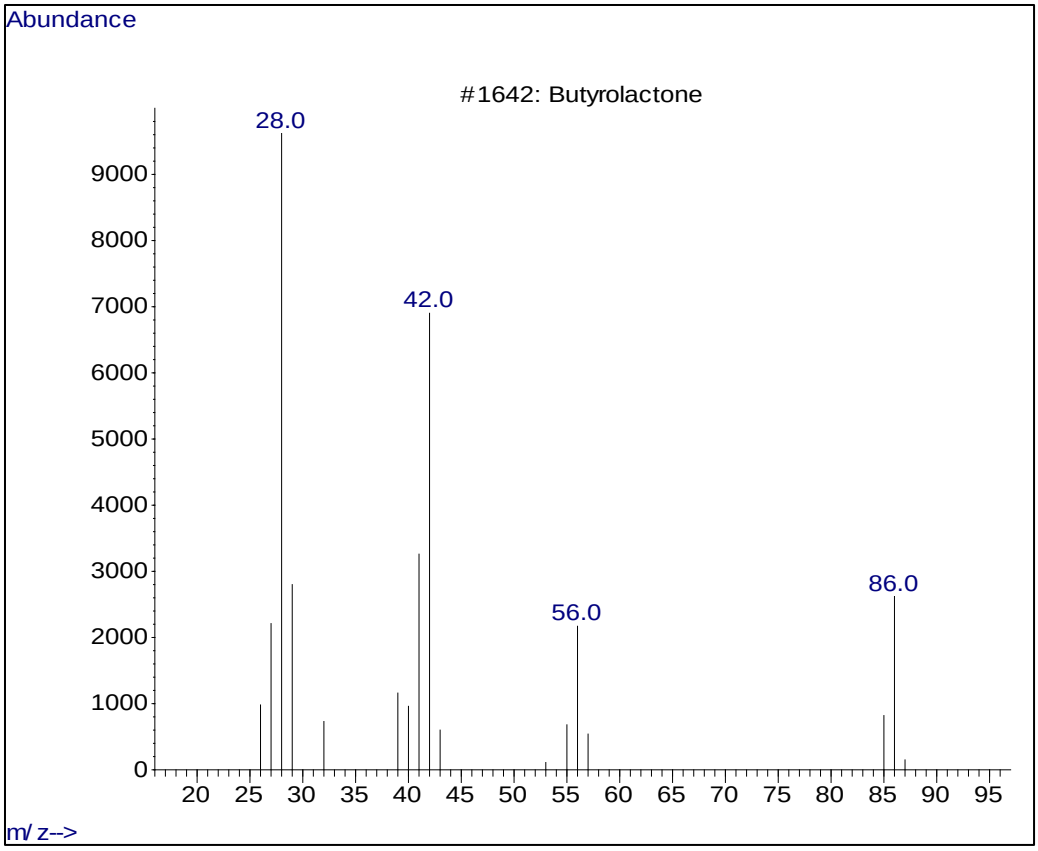


Figure 73. Reference spectrum for peak 3.

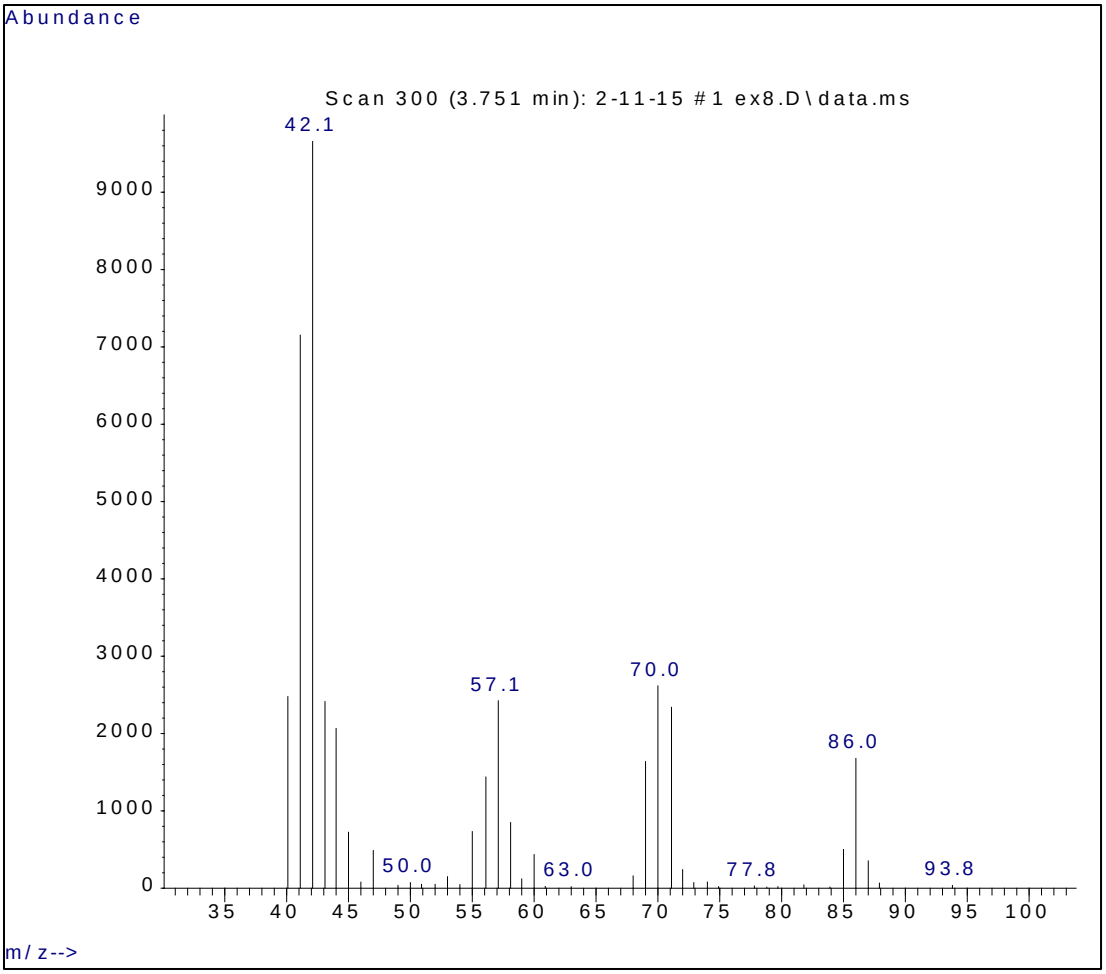


Figure 74. The identity of peak 4 is unknown. Based on its similarities to the spectra from THF derivatives encountered, it could potentially be an additional THF derivative.

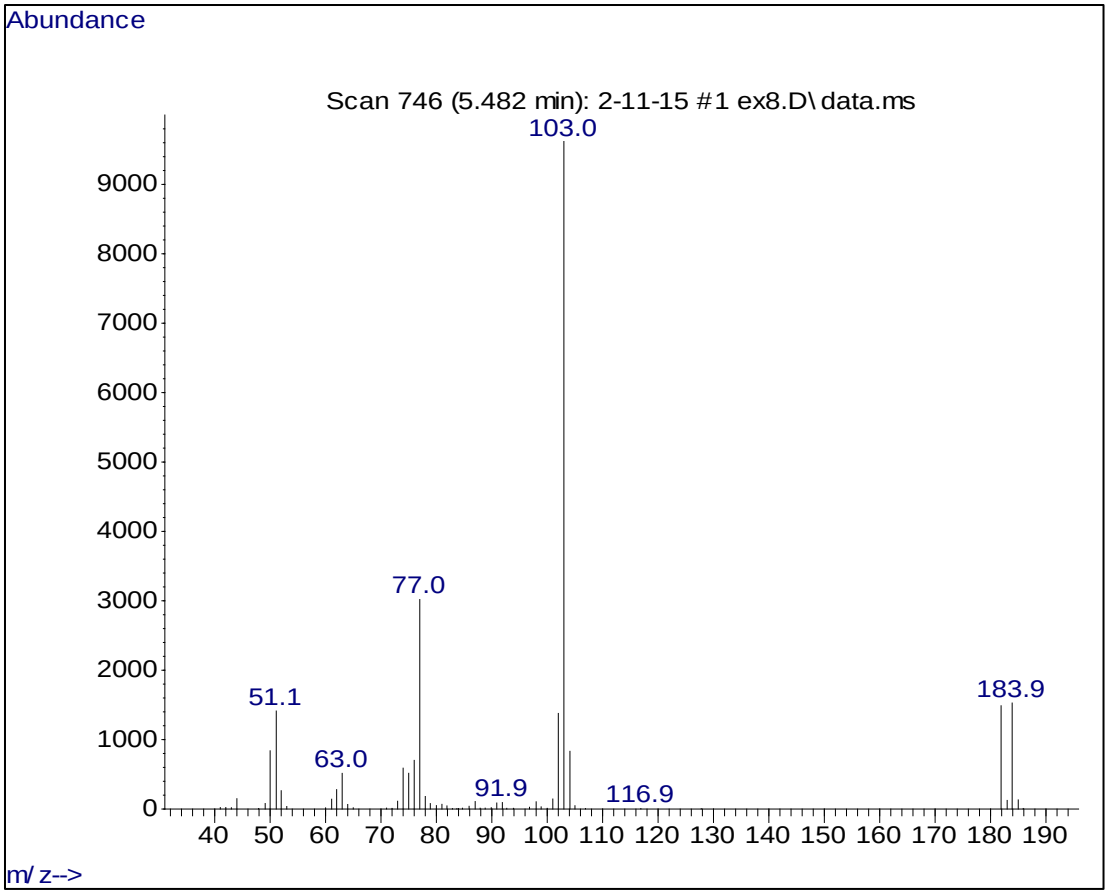


Figure 75. The identity of the peak was (1-bromoethenyl)benzene. See Figure 76 for the reference spectrum.

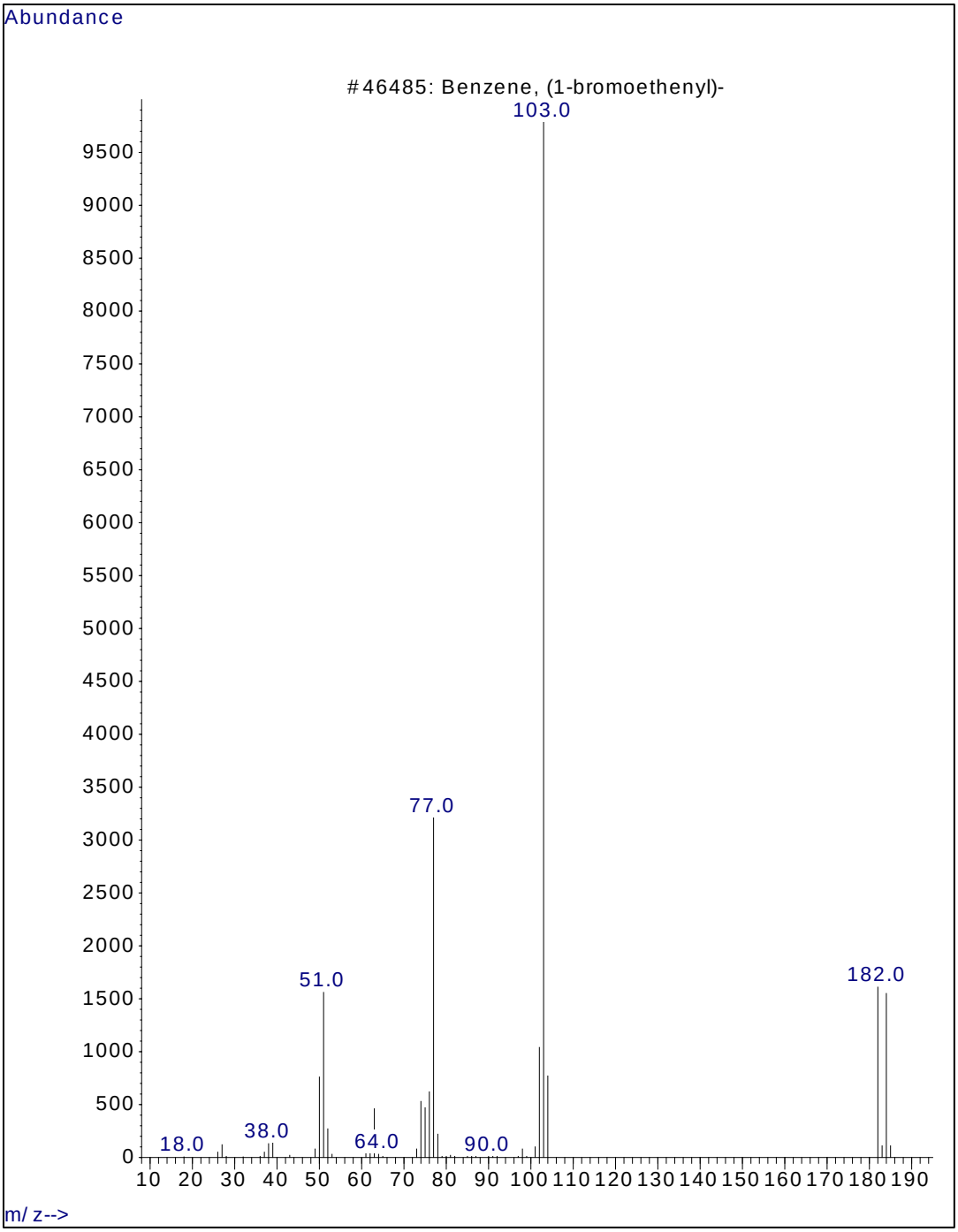


Figure 76. Reference spectrum for peak 5.

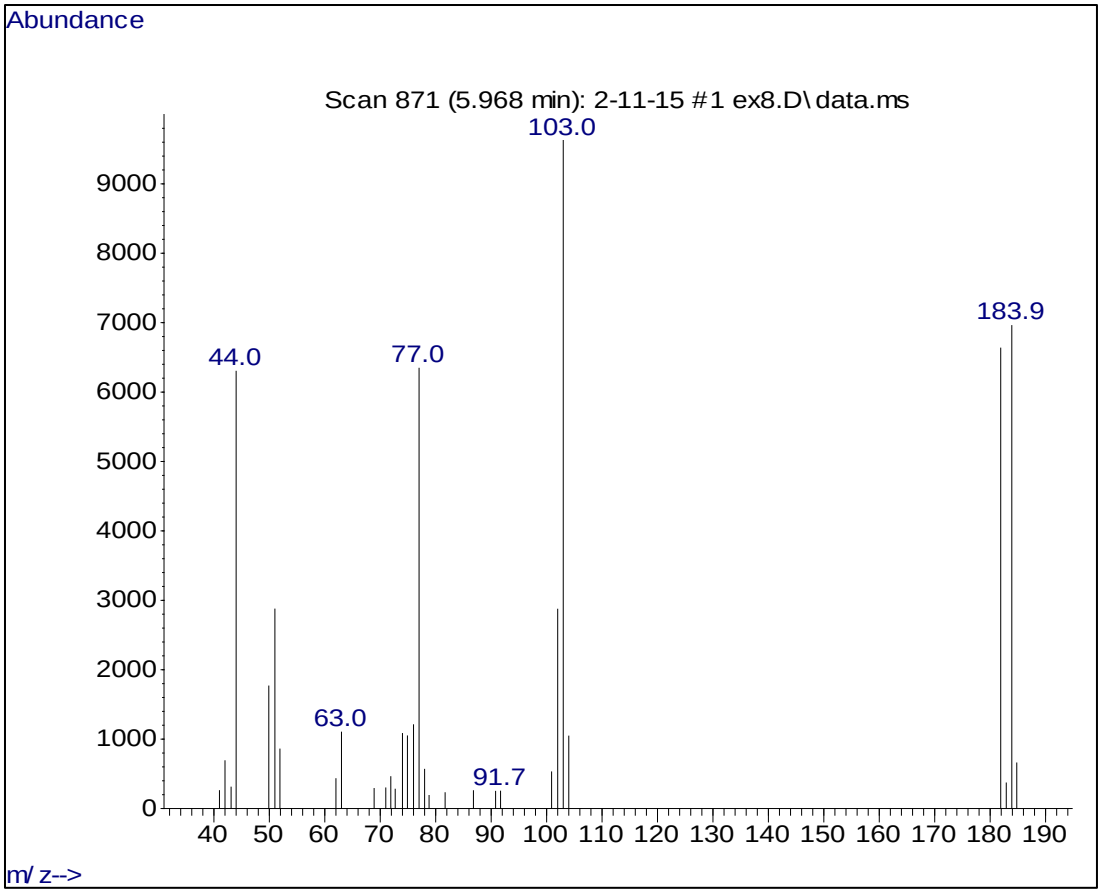


Figure 77. The identity of the peak was (2-bromoethenyl)benzene. See Figure 78 for the reference spectrum.

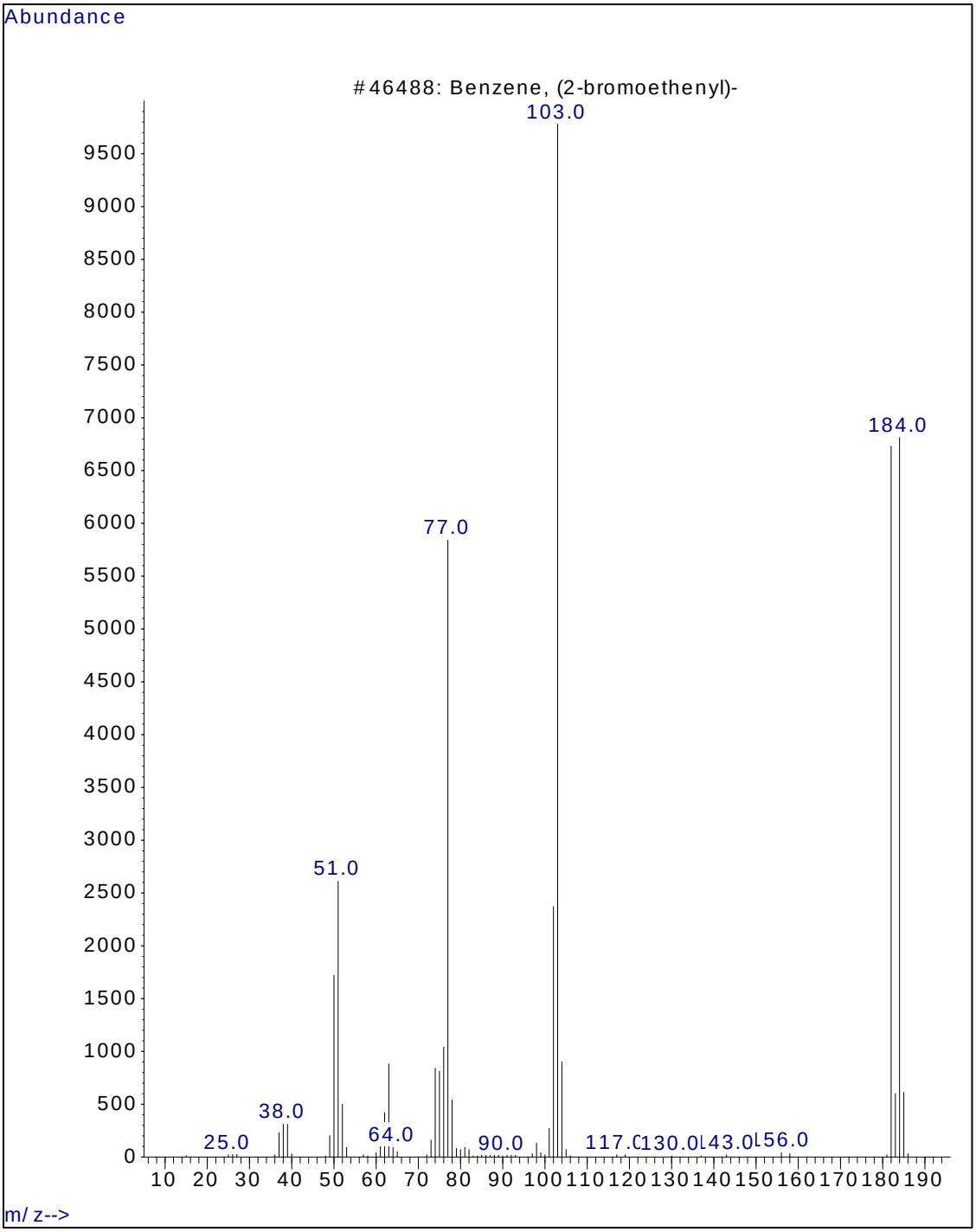


Figure 78. Reference spectrum for peak 6.

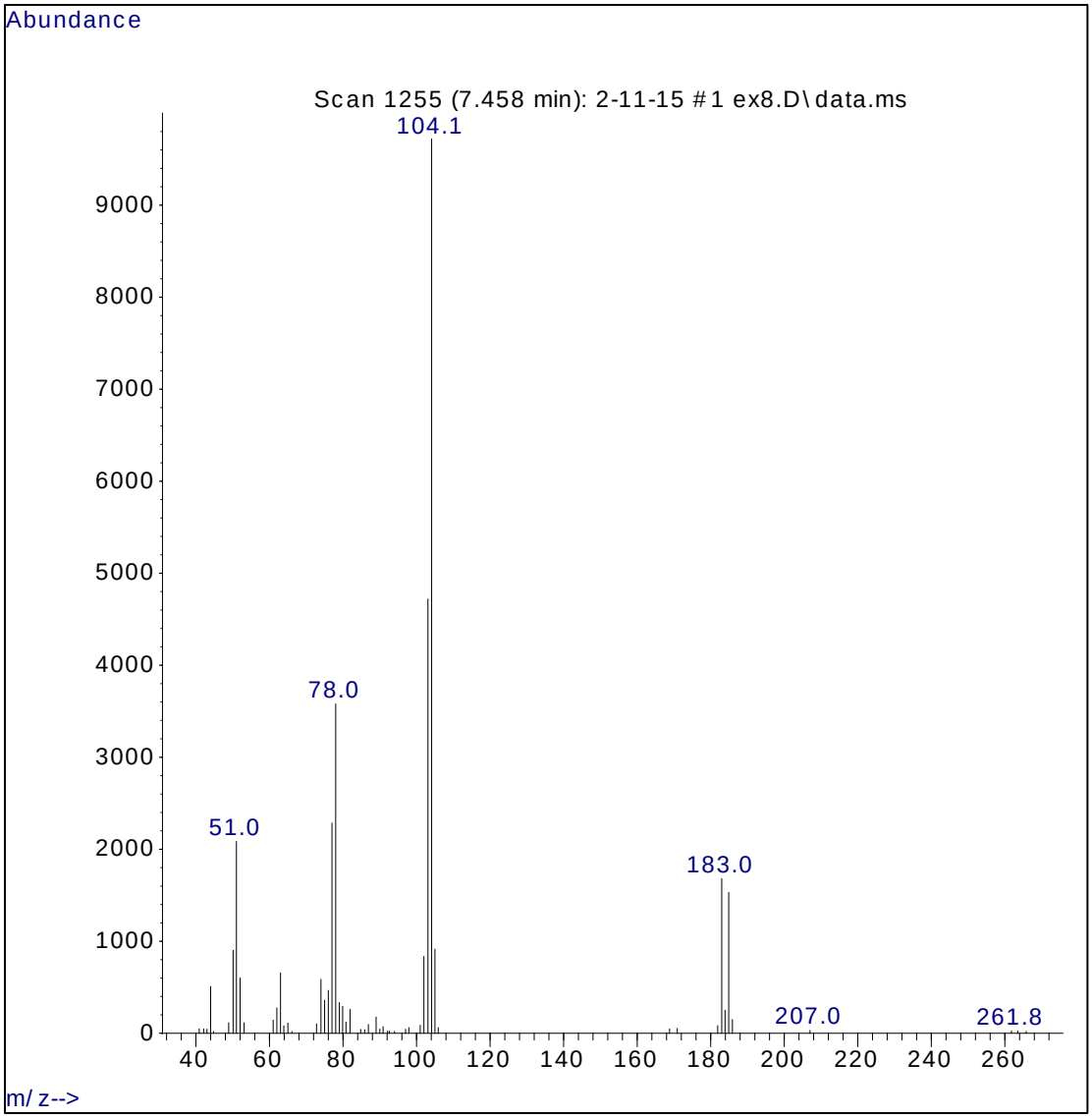


Figure 79. The identity of peak 7 was (1,2-dibromoethyl)benzene. See Figure 80 for the reference spectrum.

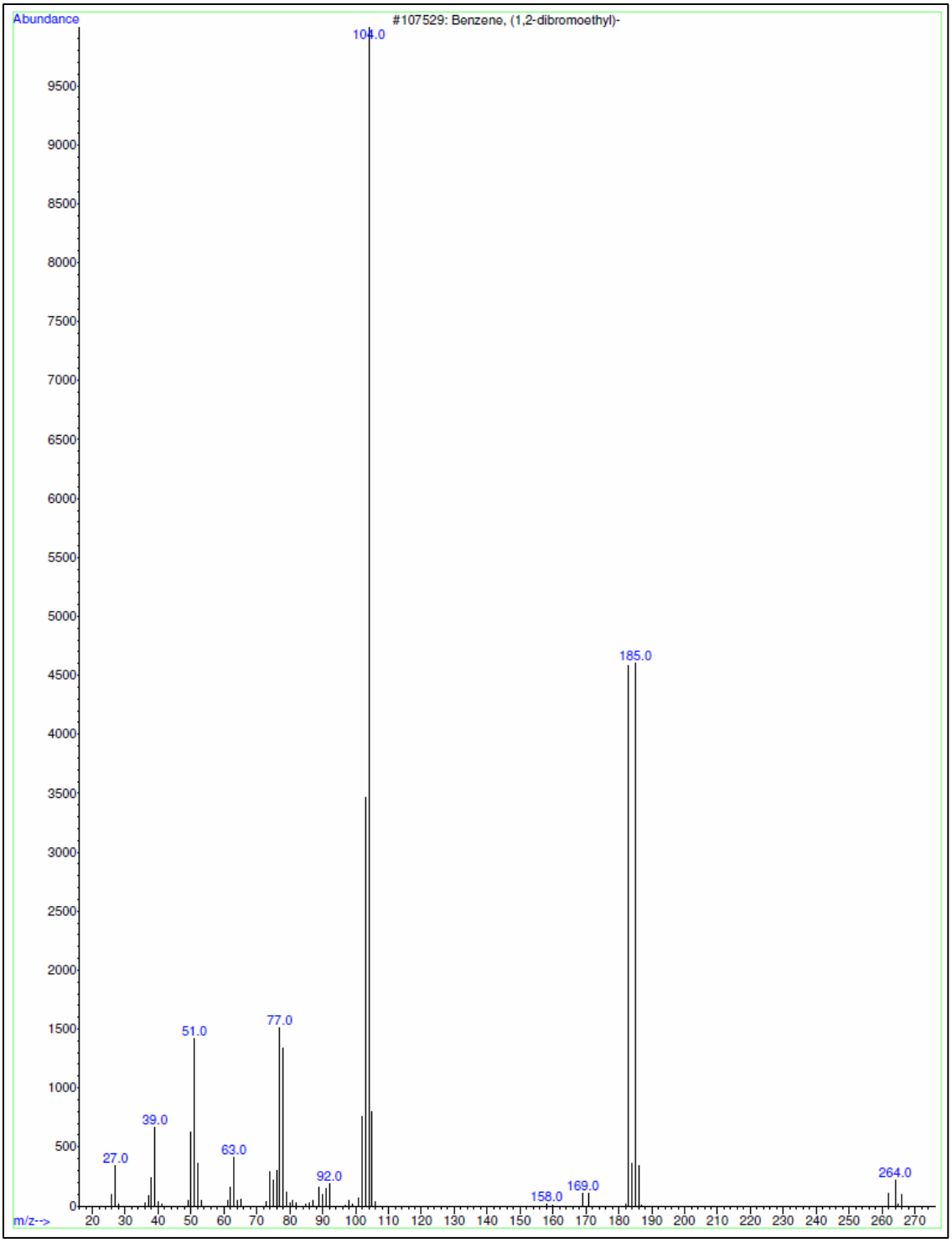


Figure 80. Reference spectrum for peak 7.

Table 9. Student data.

TA	day	time	version	preQ	postQ	change	std change
YL	Tu	5:30	1	0.875	0.5	-0.375	-0.98316
YL	Tu	5:30	1	0.5	0.875	0.375	1.0700009
YL	Tu	5:30	1	0.875	0.875	0	0.0434203
YL	Tu	5:30	1	0.5	0.875	0.375	1.0700009
YL	Tu	5:30	1	1	0.75	-0.25	-0.640967
YL	Tu	5:30	1	0.375	0.5	0.125	0.3856138
YL	Tu	5:30	1	0.5	0.875	0.375	1.0700009
YL	Tu	5:30	1	0.375	0.625	0.25	0.7278074
YL	Tu	5:30	1	1	0.75	-0.25	-0.640967
YL	Tu	5:30	1	1	0.5	-0.5	-1.325354
AC	Tu	8:00	3	1	0.75	-0.25	-0.640967
AC	Tu	8:00	3	0.75	1	0.25	0.7278074
AC	Tu	8:00	3	0.625	0.875	0.25	0.7278074
AC	Tu	8:00	3	0.5	1	0.5	1.4121944
AC	Tu	8:00	3	0.75	0.25	-0.5	-1.325354
AC	Tu	8:00	3	0.5	0.5	0	0.0434203
AC	Tu	8:00	3	0	0.625	0.625	1.7543879
AC	Tu	8:00	3	0.5	1	0.5	1.4121944
AC	Tu	8:00	3	1	0.625	-0.375	-0.98316
AC	Tu	8:00	3	0.625	0.5	-0.125	-0.298773
AC	Tu	8:00	3	0.5	0.5	0	0.0434203
AC	Tu	8:00	3	0.25	0.875	0.625	1.7543879
AC	Tu	8:00	3	0.875	0.75	-0.125	-0.298773
AC	Tu	8:00	3	0.25	0.5	0.25	0.7278074
AC	Tu	8:00	3	1	1	0	0.0434203
AC	Tu	8:00	3	0.5	0.625	0.125	0.3856138
AC	Tu	8:00	3	0.25	0.25	0	0.0434203
AC	Tu	8:00	3	1	1	0	0.0434203
AB	Fr	1:00	1	0.5	0.75	0.25	0.7278074
AB	Fr	1:00	1	0.25	0.75	0.5	1.4121944
AB	Fr	1:00	1	0	1	1	2.7809685
AB	Fr	1:00	1	0	0.75	0.75	2.0965814
AB	Fr	1:00	1	0.5	0.5	0	0.0434203
AB	Fr	1:00	1	0.25	0.375	0.125	0.3856138
AB	Fr	1:00	1	1	1	0	0.0434203
AB	Fr	1:00	1	0	0.25	0.25	0.7278074
AB	Fr	1:00	1	1	0.5	-0.5	-1.325354
AB	Fr	1:00	1	0.375	0.25	-0.125	-0.298773
AB	Fr	1:00	1	0	0.5	0.5	1.4121944

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
AB	Fr	1:00	1	0.375	1	0.625	1.7543879
AB	Fr	1:00	1	0.875	0.25	-0.625	-1.667547
AB	Fr	1:00	1	0.5	1	0.5	1.4121944
AB	Fr	1:00	1	1	1	0	0.0434203
AB	Fr	1:00	1	0.625	0.375	-0.25	-0.640967
DH	Fr	1:00	3	1	0.675	-0.325	-0.846283
DH	Fr	1:00	3	1	0.5	-0.5	-1.325354
DH	Fr	1:00	3	0.5	0.5	0	0.0434203
DH	Fr	1:00	3	1	1	0	0.0434203
DH	Fr	1:00	3	1	1	0	0.0434203
DH	Fr	1:00	3	0.875	0.5	-0.375	-0.98316
DH	Fr	1:00	3	1	0.5	-0.5	-1.325354
DH	Fr	1:00	3	1	1	0	0.0434203
DH	Fr	1:00	3	0.375	0.75	0.375	1.0700009
DH	Fr	1:00	3	0.625	0.5	-0.125	-0.298773
DH	Fr	1:00	3	0.875	1	0.125	0.3856138
DH	Fr	1:00	3	0.875	0.5	-0.375	-0.98316
DH	Fr	1:00	3	1	1	0	0.0434203
DH	Fr	1:00	3	0.375	0.5	0.125	0.3856138
DH	Fr	1:00	3	0.375	0.375	0	0.0434203
DH	Fr	1:00	3	0.5	1	0.5	1.4121944
SN	Tu	5:30	2	1	1	0	0.0434203
SN	Tu	5:30	2	0.375	0.75	0.375	1.0700009
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	0.625	-0.25	-0.640967
SN	Tu	5:30	2	1	0.5	-0.5	-1.325354
SN	Tu	5:30	2	0.25	0.375	0.125	0.3856138
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	1	0.375	-0.625	-1.667547
SN	Tu	5:30	2	0.625	0.375	-0.25	-0.640967
SN	Tu	5:30	2	0.5	0.375	-0.125	-0.298773
SN	Tu	5:30	2	0.5	0.25	-0.25	-0.640967
SN	Tu	5:30	2	0.875	1	0.125	0.3856138
SN	Tu	5:30	2	0.875	0.5	-0.375	-0.98316
DP	Tu	1:30	2	0.25	0.25	0	0.0434203
DP	Tu	1:30	2	0.375	1	0.625	1.7543879

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
DP	Tu	1:30	2	0.5	0.375	-0.125	-0.298773
DP	Tu	1:30	2	1	0.25	-0.75	-2.009741
DP	Tu	1:30	2	0.5	0.25	-0.25	-0.640967
DP	Tu	1:30	2	0.75	1	0.25	0.7278074
DP	Tu	1:30	2	1	0.5	-0.5	-1.325354
DP	Tu	1:30	2	0.5	0.625	0.125	0.3856138
DP	Tu	1:30	2	0.125	0.75	0.625	1.7543879
DP	Tu	1:30	2	1	0.5	-0.5	-1.325354
DP	Tu	1:30	2	0.625	1	0.375	1.0700009
DP	Tu	1:30	2	0.375	0	-0.375	-0.98316
DP	Tu	1:30	2	0.875	0.5	-0.375	-0.98316
DP	Tu	1:30	2	1	0.5	-0.5	-1.325354
DP	Tu	1:30	2	0.5	0.25	-0.25	-0.640967
DP	Tu	1:30	2	0.5	0.25	-0.25	-0.640967
LM	Tu	1:30	1	1	0.25	-0.75	-2.009741
LM	Tu	1:30	1	0	0.5	0.5	1.4121944
LM	Tu	1:30	1	1	0.5	-0.5	-1.325354
LM	Tu	1:30	1	0.5	0.5	0	0.0434203
LM	Tu	1:30	1	0.25	0.25	0	0.0434203
LM	Tu	1:30	1	0	0.375	0.375	1.0700009
LM	Tu	1:30	1	0.75	0.5	-0.25	-0.640967
LM	Tu	1:30	1	0.375	1	0.625	1.7543879
LM	Tu	1:30	1	1	0.25	-0.75	-2.009741
LM	Tu	1:30	1	0.625	0.75	0.125	0.3856138
LM	Tu	1:30	1	0.5	1	0.5	1.4121944
LM	Tu	1:30	1	1	0.75	-0.25	-0.640967
LM	Tu	1:30	1	1	1	0	0.0434203
LM	Tu	1:30	1	0.5	0.25	-0.25	-0.640967
LM	Tu	1:30	1	1	0.5	-0.5	-1.325354
LM	Tu	1:30	1	1	1	0	0.0434203
LM	Tu	1:30	1	1	0.5	-0.5	-1.325354
LM	Tu	1:30	1	1	1	0	0.0434203
AK	W	1:30	2	0.875	0.5	-0.375	-0.98316
AK	W	1:30	2	0.875	0.5	-0.375	-0.98316
AK	W	1:30	2	0.5	1	0.5	1.4121944
AK	W	1:30	2	0.5	0	-0.5	-1.325354
AK	W	1:30	2	0.5	1	0.5	1.4121944
AK	W	1:30	2	1	0	-1	-2.694128
AK	W	1:30	2	1	1	0	0.0434203
AK	W	1:30	2	0.375	1	0.625	1.7543879

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
AK	W	1:30	2	1	1	0	0.0434203
AK	W	1:30	2	0.625	0.5	-0.125	-0.298773
AK	W	1:30	2	1	1	0	0.0434203
AK	W	1:30	2	1	1	0	0.0434203
AK	W	1:30	2	1	1	0	0.0434203
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
LM	Tu	8:00	3	1	0.5	-0.5	-1.325354
LM	Tu	8:00	3	0.5	0.625	0.125	0.3856138
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
LM	Tu	8:00	3	0.5	0.75	0.25	0.7278074
LM	Tu	8:00	3	1	0.5	-0.5	-1.325354
LM	Tu	8:00	3	1	0.75	-0.25	-0.640967
LM	Tu	8:00	3	0.375	0.5	0.125	0.3856138
LM	Tu	8:00	3	0.375	0.5	0.125	0.3856138
LM	Tu	8:00	3	1	0.375	-0.625	-1.667547
LM	Tu	8:00	3	0.5	1	0.5	1.4121944
LM	Tu	8:00	3	0.5	0.625	0.125	0.3856138
LM	Tu	8:00	3	0.75	0.25	-0.5	-1.325354
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
LM	Tu	8:00	3	0.5	0.5	0	0.0434203
YS	W	8:00	3	0.5	0.75	0.25	0.7278074
YS	W	8:00	3	0.875	0.25	-0.625	-1.667547
YS	W	8:00	3	1	0.5	-0.5	-1.325354
YS	W	8:00	3	1	0.5	-0.5	-1.325354
YS	W	8:00	3	0.5	1	0.5	1.4121944
YS	W	8:00	3	1	0.375	-0.625	-1.667547
YS	W	8:00	3	0.375	0.375	0	0.0434203
YS	W	8:00	3	0.5	0.5	0	0.0434203
YS	W	8:00	3	0.5	0.5	0	0.0434203
YS	W	8:00	3	1	1	0	0.0434203
YS	W	8:00	3	1	0.5	-0.5	-1.325354
YS	W	8:00	3	1	0.375	-0.625	-1.667547
YS	W	8:00	3	0.5	0.875	0.375	1.0700009
YS	W	8:00	3	0.875	0.375	-0.5	-1.325354
YS	W	8:00	3	0.25	1	0.75	2.0965814
YS	W	8:00	3	1	1	0	0.0434203
YS	W	8:00	3	0.5	0.75	0.25	0.7278074
YS	W	8:00	3	1	0.5	-0.5	-1.325354

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
YS	W	8:00	3	0.375	0.875	0.5	1.4121944
AC	Th	8:00	2	0.25	1	0.75	2.0965814
AC	Th	8:00	2	0.25	1	0.75	2.0965814
AC	Th	8:00	2	1	0.25	-0.75	-2.009741
AC	Th	8:00	2	0.5	0.25	-0.25	-0.640967
AC	Th	8:00	2	0.25	0.25	0	0.0434203
AC	Th	8:00	2	0.75	0.5	-0.25	-0.640967
AC	Th	8:00	2	0.5	0.75	0.25	0.7278074
AC	Th	8:00	2	0.5	0.25	-0.25	-0.640967
AC	Th	8:00	2	0.375	0	-0.375	-0.98316
AC	Th	8:00	2	0.875	0.5	-0.375	-0.98316
AC	Th	8:00	2	0.25	0	-0.25	-0.640967
AC	Th	8:00	2	0.75	0.5	-0.25	-0.640967
AC	Th	8:00	2	0.375	0.5	0.125	0.3856138
AC	Th	8:00	2	1	0.875	-0.125	-0.298773
AC	Th	8:00	2	0.5	0.25	-0.25	-0.640967
AC	Th	8:00	2	1	0.75	-0.25	-0.640967
AC	Th	8:00	2	1	0.5	-0.5	-1.325354
RD	Th	5:30	1	0.5	0.875	0.375	1.0700009
RD	Th	5:30	1	0.5	0.75	0.25	0.7278074
RD	Th	5:30	1	1	0.75	-0.25	-0.640967
RD	Th	5:30	1	1	0.375	-0.625	-1.667547
RD	Th	5:30	1	0.5	0.25	-0.25	-0.640967
RD	Th	5:30	1	0.875	0.25	-0.625	-1.667547
RD	Th	5:30	1	0.5	0.5	0	0.0434203
RD	Th	5:30	1	0.5	1	0.5	1.4121944
RD	Th	5:30	1	0.875	0.25	-0.625	-1.667547
RD	Th	5:30	1	0.25	0.5	0.25	0.7278074
RD	Th	5:30	1	0.5	0.25	-0.25	-0.640967
RD	Th	5:30	1	0.25	0.5	0.25	0.7278074
RD	Th	5:30	1	1	1	0	0.0434203
RD	Th	5:30	1	1	1	0	0.0434203
RD	Th	5:30	1	0.25	0.25	0	0.0434203
RD	Th	5:30	1	1	0.875	-0.125	-0.298773
RD	Th	5:30	1	0.25	0.5	0.25	0.7278074
RD	Th	5:30	1	1	0.625	-0.375	-0.98316
YL	Th	5:30	2	0.25	0.75	0.5	1.4121944
YL	Th	5:30	2	0.5	1	0.5	1.4121944
YL	Th	5:30	2	0.5	1	0.5	1.4121944
YL	Th	5:30	2	1	1	0	0.0434203

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
YL	Th	5:30	2	1	1	0	0.0434203
YL	Th	5:30	2	1	1	0	0.0434203
YL	Th	5:30	2	1	0.375	-0.625	-1.667547
YL	Th	5:30	2	0.5	0.25	-0.25	-0.640967
YL	Th	5:30	2	1	1	0	0.0434203
YL	Th	5:30	2	0.75	0.5	-0.25	-0.640967
YL	Th	5:30	2	0.625	0.5	-0.125	-0.298773
YL	Th	5:30	2	0.625	0.75	0.125	0.3856138
YL	Th	5:30	2	0.875	1	0.125	0.3856138
YL	Th	5:30	2	1	1	0	0.0434203
YL	Th	5:30	2	1	0.375	-0.625	-1.667547
DP	Th	1:30	3	0.875	0.5	-0.375	-0.98316
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	1	1	0	0.0434203
DP	Th	1:30	3	0.75	1	0.25	0.7278074
DP	Th	1:30	3	0.5	0.75	0.25	0.7278074
DP	Th	1:30	3	0.875	1	0.125	0.3856138
DP	Th	1:30	3	0.875	1	0.125	0.3856138
DP	Th	1:30	3	0.5	0.375	-0.125	-0.298773
DP	Th	1:30	3	1	0.5	-0.5	-1.325354
DP	Th	1:30	3	0.75	1	0.25	0.7278074
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	0.25	0.5	0.25	0.7278074
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	0.625	0.5	-0.125	-0.298773
DP	Th	1:30	3	0.5	0.25	-0.25	-0.640967
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	0.5	0.5	0	0.0434203
DP	Th	1:30	3	0.5	0.75	0.25	0.7278074
HH	W	1:30	3	0.875	0.75	-0.125	-0.298773
HH	W	1:30	3	0.875	1	0.125	0.3856138
HH	W	1:30	3	0.875	1	0.125	0.3856138
HH	W	1:30	3	0.375	0.875	0.5	1.4121944
HH	W	1:30	3	0.5	0.5	0	0.0434203
HH	W	1:30	3	0.5	0.625	0.125	0.3856138
HH	W	1:30	3	0.5	1	0.5	1.4121944
HH	W	1:30	3	0.75	0.875	0.125	0.3856138
HH	W	1:30	3	1	1	0	0.0434203
HH	W	1:30	3	1	1	0	0.0434203

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
HH	W	1:30	3	1	0.5	-0.5	-1.325354
HH	W	1:30	3	0.5	0.5	0	0.0434203
HH	W	1:30	3	1	0.5	-0.5	-1.325354
HH	W	1:30	3	0.5	0.875	0.375	1.0700009
HH	W	5:30	3	0.375	1	0.625	1.7543879
HH	W	5:30	3	0.5	0.5	0	0.0434203
HH	W	5:30	3	1	0.25	-0.75	-2.009741
HH	W	5:30	3	0.25	1	0.75	2.0965814
HH	W	5:30	3	0.25	1	0.75	2.0965814
HH	W	5:30	3	0.5	0.5	0	0.0434203
HH	W	5:30	3	0.875	0.75	-0.125	-0.298773
HH	W	5:30	3	0.5	0.25	-0.25	-0.640967
HH	W	5:30	3	1	1	0	0.0434203
HH	W	5:30	3	0.875	0.5	-0.375	-0.98316
HH	W	5:30	3	0.5	1	0.5	1.4121944
HH	W	5:30	3	0.75	0.5	-0.25	-0.640967
HH	W	5:30	3	0.75	1	0.25	0.7278074
HH	W	5:30	3	0.375	0.5	0.125	0.3856138
HH	W	5:30	3	0.25	0.5	0.25	0.7278074
HH	W	5:30	3	0.5	0.375	-0.125	-0.298773
HH	W	5:30	3	0.5	1	0.5	1.4121944
HH	W	5:30	3	0.875	0.5	-0.375	-0.98316
MW	W	5:30	1	0.5	1	0.5	1.4121944
MW	W	5:30	1	0.375	0.5	0.125	0.3856138
MW	W	5:30	1	1	0.75	-0.25	-0.640967
MW	W	5:30	1	0.25	0.5	0.25	0.7278074
MW	W	5:30	1	0.25	0.25	0	0.0434203
MW	W	5:30	1	0.5	0.5	0	0.0434203
MW	W	5:30	1	0.5	0.375	-0.125	-0.298773
MW	W	5:30	1	1	0.875	-0.125	-0.298773
MW	W	5:30	1	1	0.5	-0.5	-1.325354
MW	W	5:30	1	1	0.5	-0.5	-1.325354
MW	W	5:30	1	0.5	0.375	-0.125	-0.298773
MW	W	5:30	1	0.25	0.375	0.125	0.3856138
MW	W	5:30	1	0.5	0.5	0	0.0434203
MW	W	5:30	1	0.25	0.625	0.375	1.0700009
MW	W	5:30	1	0.5	0.25	-0.25	-0.640967
MW	W	5:30	1	1	0.625	-0.375	-0.98316
MW	W	5:30	1	0.25	0.375	0.125	0.3856138
MW	W	5:30	1	1	0.375	-0.625	-1.667547

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
NH	F	8:00	1	0.875	1	0.125	0.3856138
NH	F	8:00	1	0.5	0.375	-0.125	-0.298773
NH	F	8:00	1	0.5	0.875	0.375	1.0700009
NH	F	8:00	1	0.5	1	0.5	1.4121944
NH	F	8:00	1	0.25	0.375	0.125	0.3856138
NH	F	8:00	1	0.875	0.625	-0.25	-0.640967
NH	F	8:00	1	1	0.5	-0.5	-1.325354
NH	F	8:00	1	1	0.625	-0.375	-0.98316
NH	F	8:00	1	0.75	0.5	-0.25	-0.640967
NH	F	8:00	1	1	1	0	0.0434203
NH	F	8:00	1	0.75	0.875	0.125	0.3856138
NH	F	8:00	1	0.125	0.25	0.125	0.3856138
NH	F	8:00	1	0.625	0.375	-0.25	-0.640967
NH	F	8:00	1	0.375	1	0.625	1.7543879
YS	F	8:00	1	0.375	1	0.625	1.7543879
YS	F	8:00	1	0.375	0.5	0.125	0.3856138
YS	F	8:00	1	0.875	0.875	0	0.0434203
YS	F	8:00	1	0.375	0.875	0.5	1.4121944
YS	F	8:00	1	0	0.25	0.25	0.7278074
YS	F	8:00	1	0	0.25	0.25	0.7278074
YS	F	8:00	1	0.125	1	0.875	2.438775
YS	F	8:00	1	0.625	1	0.375	1.0700009
YS	F	8:00	1	0.375	0.75	0.375	1.0700009
YS	F	8:00	1	1	0.375	-0.625	-1.667547
YS	F	8:00	1	0.875	0.5	-0.375	-0.98316
YS	F	8:00	1	0.625	0.75	0.125	0.3856138
YS	F	8:00	1	0.5	0.875	0.375	1.0700009
YS	F	8:00	1	0	0.25	0.25	0.7278074
YS	F	8:00	1	0.875	0.5	-0.375	-0.98316
YS	F	8:00	1	0.5	0.375	-0.125	-0.298773
YS	F	8:00	1	1	0.5	-0.5	-1.325354
YS	F	8:00	1	0.675	1	0.325	0.9331235
YS	Th	8:00	2	0.5	0.375	-0.125	-0.298773
YS	Th	8:00	2	1	1	0	0.0434203
YS	Th	8:00	2	0.75	1	0.25	0.7278074
YS	Th	8:00	2	0.25	0.875	0.625	1.7543879
YS	Th	8:00	2	1	0.125	-0.875	-2.351934
YS	Th	8:00	2	1	1	0	0.0434203
YS	Th	8:00	2	0	0.25	0.25	0.7278074
YS	Th	8:00	2	0.5	0.25	-0.25	-0.640967

continued

Table 9: continued

TA	day	time	version	preQ	postQ	change	std change
YS	Th	8:00	2	1	1	0	0.0434203
YS	Th	8:00	2	0.25	0.25	0	0.0434203
YS	Th	8:00	2	0.875	0.625	-0.25	-0.640967
YS	Th	8:00	2	0.375	1	0.625	1.7543879
YS	Th	8:00	2	0.5	0	-0.5	-1.325354
YS	Th	8:00	2	0.5	1	0.5	1.4121944
YS	Th	8:00	2	0.875	0.25	-0.625	-1.667547
YS	Th	8:00	2	0.875	0.25	-0.625	-1.667547
YS	Th	8:00	2	0.375	0.25	-0.125	-0.298773
YS	Th	8:00	2	1	0.625	-0.375	-0.98316
YS	Th	8:00	2	0.375	0.5	0.125	0.3856138
YS	Th	8:00	2	0.75	0.875	0.125	0.3856138